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Metallic gold thin film micropattern on polydimethylsiloxanefilm for flexible electronic sensors and circuits

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Abstract: This work illustrates the importance as well as major challenges related to the development of malleable metallic Au thin film micropattern on soft elastomeric film and then presents a fabrication technique to overcome these challenges for developing reliable, flexible electronic sensors and circuits. A self-assembled molecular adhesive layer has been introduced between the polydimethylsiloxane (PDMS) and the thin metal film to increase the adhesion and then analyzed the multilayer structure. The contact angle measurement showed that the introduction (3-mercaptopropyl) trimethoxysilane (MPTMS) molecular adhesive layer increases the hydrophilicity of the PDMS film for a more extended period and Au film on MPTMS coated PDMS shows superior film quality. The random buckles formed on the thin Au film have been successively manipulated using controlled heating after micropatterning. The SEM analysis of the Au thin film confirmed that the deposited film is granular and filled with nanogaps. The electrical characterization of the deposited showed that the sheet resistance of the metal thin is higher compared to the Au thin film on Si surface. This investigation is beneficial for realizing reliable, flexible electronic devices and circuits on soft polymer.

Keywords: *Contact angle, flexible sensor, microfabrication, microstructure, optical lithography, PDMS,*

INTRODUCTION

Recent advancements in the field of flexible electronic sensors and systems demand thin metal film to be fabricated on a flexible or a stretchable substrate for sensing elements as well as connecting circuits[1]. Flexible sensors with unique stretchability have vast potential applications in various fields such as health monitoring, man-machine interface, robotic skin, wearable devices, etc.[2,3,4]. Au is a highly conductive biocompatible ductile noble metal and is suitable for thin film microstructure on soft elastomeric material. Similarly, PDMS is an established elastomeric MEMS material and compatible with most of the traditional microfabrication processes[5]. Moreover, PDMS is a highly flexible, relatively cheap, chemically nonreactive biocompatible soft material that makes it a prominent material for biomedical and electronic skin applications [6,7]. Although the Au strain gauge sensor developed on PDMS film shows much higher sensitivity due to low Young's modus of the substrate film, it also faces three significant problems. First, the high strain sensitivity of these sensors is driven by the formation of microcracks in a direction perpendicular to its stretching, which creates some local debonding of the film from the elastomer substrate [8]. Although this debonding is local and has less impact on reversibility, it influences the linearity of the strain response. Second, miniaturization of the resistor becomes critical as the width of the resistor film must always be broader than the microcrack dimension. Third, the Au thin film fabricated on an elastomeric film has random buckles on its surface[5]. Thus, the formation of a crack on a randomly oriented film becomes a complex shape and will contribute to nonlinear strain response behavior[9]. Moreover, PDMS is a hydrophobic in nature and the thin metal film deposited on its film has poor adhesion. Therefore, any electronic device developed with these material shows poor reliability, especially in flexible and stretchable applications [10]. Therefore, reliable thin metal thin film deposition on PDMS film becomes critical for maintaining the quality of any fabricated electronic devices. In this work, we deposit Cr/Au film on PDMS film coated with a molecular adhesive layer and then study the quality of the film and simultaneously try to fabricate an array Au thin film microelectrode with connecting microlines on PDMS film. Moreover, manipulation of the random buckles by heat treatment will be investigated for the reliable microelectronic device.

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EXPERIMENTAL PROCEDURES

Substrate preparation

A 150 μm thick PDMS film was prepared with Sylgard 184 kit from Dow Corning Corp. by thoroughly mixing the base and curing solution (10:1) and spin coating over a glass slide at a speed of 500 rpm for 20s. The sample was cured by heating the sample at 90ºC for two hours. A 2 μm thick polyvinyl alcohol (PVA) was used as a sacrificial layer between the glass slide and the PDMS film. The cured PDMS film was treated with O_2 plasma at 150 mTorr chamber pressure, 40 W plasma power for 30 s and subsequently immersed in a 5 mM solution of (MPTMS) for one hour. The MPTMS coting was used as a molecular adhesive layer for reliable metal thin film over hydrophobic PDMS substrate film[11]. The sample was rinsed in deionized water(DI) and dried by blowing N_2 gas. The hydrophilicity of the MPTMS coated PDMS was tested and compared with bare PDMS film, and only O_2 plasma-treated PDMS film.

Thin-film deposition

The Au material was sputtered on the top of the Cr layer over the surface-modified PDMS sample. The base vacuum of the sputtering chamber was kept below 3×10^{-6} mbar of pressure before Ar gas was injected into the deposition chamber. The chamber was first flushed with Ar gas and then maintained a constant Ar pressure of 2.6×10^{-3} mbar for the entire period of deposition. The PDMS samples were kept at 2.36″ above the target material on the substrate holder plate. Both Cr and Au target material have 4″ diameters and 99.99% purity.

Microstructure patterning

The Cr and Au thin film sputtered over PDMS film were micropatterned with a conventional photolithography technique. The fabrication process starts with coating positive photoresist (HPR 504, from Fujifilm) on the PDMS sample using a spin coater (3000 rpm for 20s) followed by soft baking at 90°C for 30 min. The sample was subsequently exposed to UV light inside a Mask aligner (Karl Suss MJB3 Mask Aligner) for 7.5 sec. The exposed samples were then developed in a developer solution hard 429 (Fujifilm). The samples were subsequently post baked at 120°C for 25 min for hardening the patterned photoresist. The Au and then Cr thin films were sequentially removed by immersing in Au and Cr etchant (Transene), respectively. The remaining photoresist was removed by dipping in acetone followed by cleaning in deionized water and then dried with N_2 gas. The PDMS samples were then heated at 160°C for 15 min and then cooled down to room temperature for allowing the random buckles developed due to mismatch Young's modulus during the sputtering process to an ordered parallel structure[9]. The PDMS film was released by immersing in hot water (60°C, 2 hours) from the underlying glass substrate. Finally, the micropatterned film was dried with N_2 gas and prepared for characterization.

Testing and Characterization

The contact angle was measured by capturing the image of the water droplet by a high-resolution CCD camera and 'Screen Protractor' software. The surface morphology of the Au thin film was analyzed by both optical (Leica DM2700M)and scanning electron microscope (Zeiss Sigma FE-SEM -03-85). The sheet resistance of the deposited Au film was measured with the four-probe technique, and the thickness of the film was measured with a surface profiler (DEKTAK150).

RESULTS

Contact Angle measurement

In order to study the effect of liquid deposited MPTMS layer on the surface energy of the PDMS film, static contact angle measurement experiment was performed using the sessile drop method after liquid deposition. The samples were thoroughly dried using an N_2 blower before placing a 4-6 μL of deionized (resistivity 18 MΩ cm)

water droplet on its surface for the hydrophobicity/hydrophilicity test. The contact angle of MPTMS deposited PDMS was compared with untreated PDMS (freshly prepared PDMS sample without surface modification), and O_2 plasma (150 mTorr, plasma power 40 W, for 30s of time) treated PDMS sample. As the surface free energy of solid is associated with the chemical composition on its surface [11], the variation of the contact angle reflects the change in chemical composition on its surface. When the PDMS surface was exposed under O_2 plasma, the hydrophobic surface temporarily becomes hydrophilic [11]. Therefore, a variation of the contact angle was measured at a different time interval after surface modification. Variation of the measured contact angle for similar samples is plotted with an error bar and is shown in figure 1. The experiment was performed with three samples at a time for each of the three sets. The measured contact angle of a liquid droplet on the liquid MPTMS layer deposited PDMS was found to be 28° after 10 min and saturates at 37±3° after 5 hours of surface treatment. The O_2 plasma-treated PDMS sample has shown hydrophilic nature just after plasma treatment and becomes hydrophobic with a contact angle of 92±3° after 2 hours. The water droplet contact angle on bare PDMS was observed at 108±3° throughout that period.

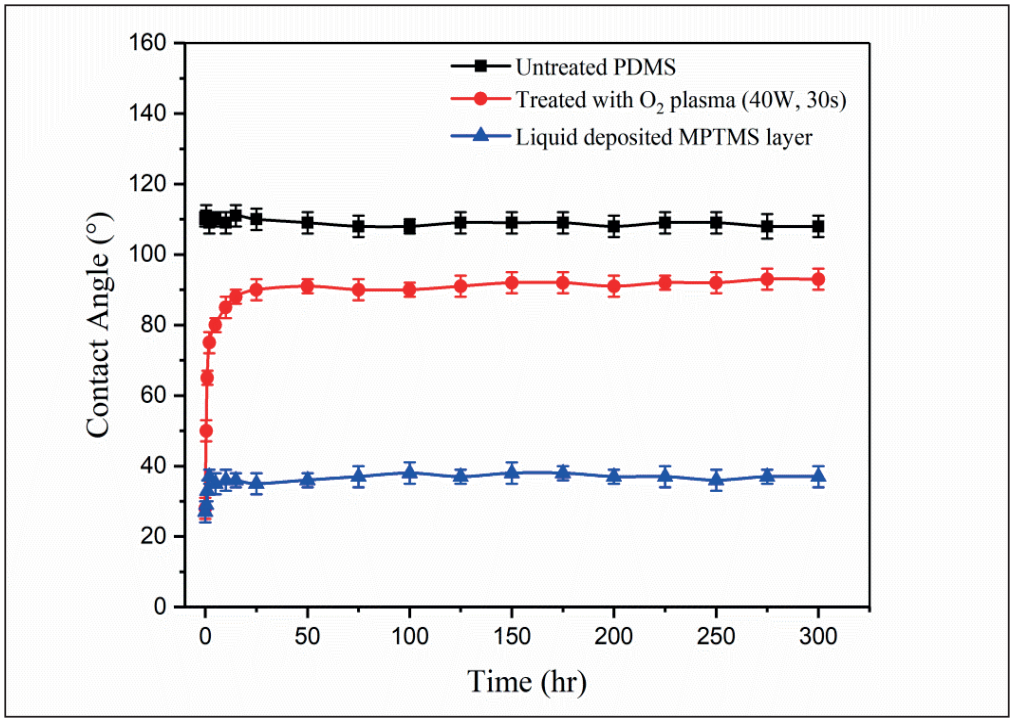

Fig. 1: Variation of contact angle of a water droplet at different time intervals for untreated PDMS, O_2 plasma-treated PDMS, and MPTMS layer deposited PDMS sample.

Thin-film adhesion study

To observe the adhesion between the deposited metal film on PDMS macroscopic adhesion experiment was performed. The test was conducted using two different adhesive tapes; tape 1 has low adhesion compared to Tape 2 and thus could be released easily from the deposited Au surface. The adhesion tests were performed for sputtered deposited Au film, Cr/Au film on O_2 plasma-treated PDMS, and Cr/Au film on MPTMS layer deposited PDMS. Figure 3 shows the optical images of the transfer of Au film to the adhesive tapes after peeling up from its surface. It is quite clear from the experimental results that the Au thin film on PDMS substrate has the lowest adhesion compared to the other two films. It is observed that introducing intermediate Cr film increases the adhesion of the Au thin film, and the sample was able to clear the Tape 1 test but fails in the Tape 2 test. On the other hand, sputtered Cr/Au film on MPTMS layer deposited PDMS film qualifies both the test. The macroscopic adhesion test results support the published works, which suggest that introducing MPTMS molecular adhesive layer increases the adhesion between the PDMS and the thin metal film.

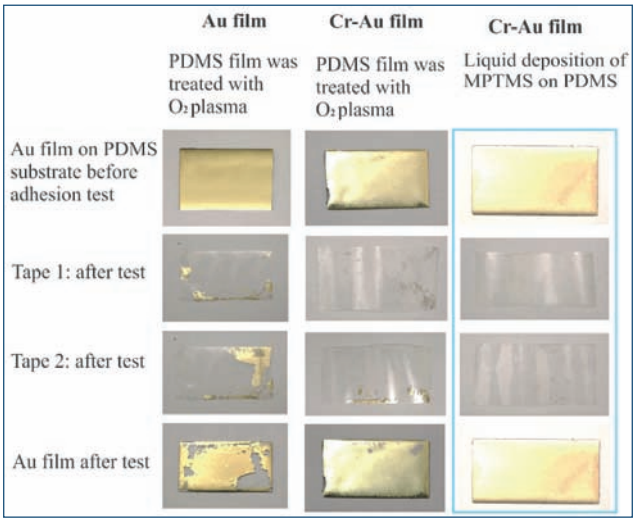

Fig. 2 : Photograph of the Au thin film over PDMS before and after the double tape test on O_2 plasma-treated sample, Cr/Au film on O_2 plasma-treated sample, and MPTMS coated sample.

Bucklemanipulation study

The fabricated Cr/Au thin film microstructure on PDMS with magnified images at the contact pad and central microline region of a single resistor is shown in figure 3. The magnified images show that the formation of ordered buckles on the surface of the metal film resistor. The ordered buckles after heating the patterned structure can be explained by studying the various stresses associated with the fabrication process. In this process, the Cr/Au thin film was deposited on a smooth PDMS film at 60°C using sputtering, which cooled down to 25°C after deposition. The deposited metal film experiences an equibiaxial compressive during this process due to different coefficients of thermal expansion of the PDMS and metal film, leading to random buckles [9]. After pattering the thin film using photolithography process, the length and the width of microline changes. The subsequent heating to 160°C and cooling made the equibiaxial stress to became directional, i.e., compressive stress along the width of the microline is different from the length[9]. This directional stress forces the buckles to transform into an ordered structure on the metal surface. Therefore, this method does not require any rigid structure or pre-strained PDMS film for ordering the random buckles [13] that formed due to mismatch Young's modulus and coefficient of thermal expansion after deposition.

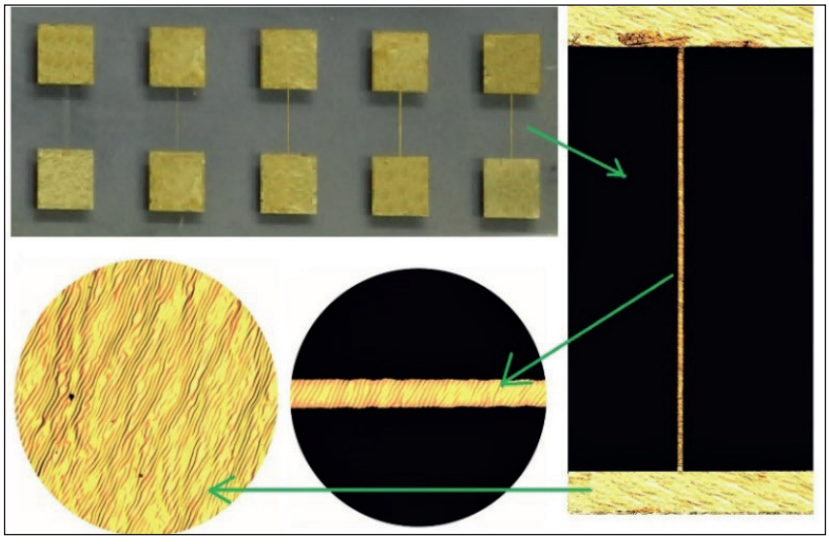

Fig. 3: Optical micrograph of Au thin film microline on a flexible PDMS substrate with magnified images of a micro-resistor.

Electrical characteristics study

The details of the optimized deposition conditions and electrical properties are presented in table 1. It is observed that at constant deposition, the film thickness increases linearly with the sputtering time on the PDMS sample. The results indicate that the measured sheet resistance of the Au film is higher than the bulk metal[9]. The experimental results also show that an increase in the film thickness exponentially decreases the sheet resistance of the Au film, which resembles the reported literature[14]. The Au thin film surface deposited over the PDMS film using dc magnetron sputtering is shown in figure 4. This SEM image shows that the surface of the Au film is granular, and the average diameter of the grain size is ~40 nm. The Au thin film surface is filled with nanoholes and nanocracks in between these grains. This nanohole and nanogaps are responsible for the high resistivity of the thin Au film on the elastomeric substrate compared to a bulk Au film[8]. When tensile strain is applied on a strain sensor with Au thin film as a resistor on PDMS film, the nano-cracks between granular islands widens and contribute to high normalized resistance, and suitable for high strain sensitivity.

Table 1: The deposition parameters of Cr/Au sputtering & film properties.

Film type	Working pressure (mbar)	Sputtering power (W)	Sputtering time (s)	Film thickness (nm)	Sheet resistance Ω / €
Cr	0.0025	54	40	3.15 ± 0.5	
			60	5.05 ± 0.6	
Au	0.0025	60	150	102 ± 2.5	1.843 ± 0.285
			180	118 ± 3.0	1.035 ± 0.250
			230	154 ± 4.5	0.48 ± 0.115
			270	183 ± 4.0	0.331 ± 0.055
			300	202 ± 4.5	0.265 ± 0.045

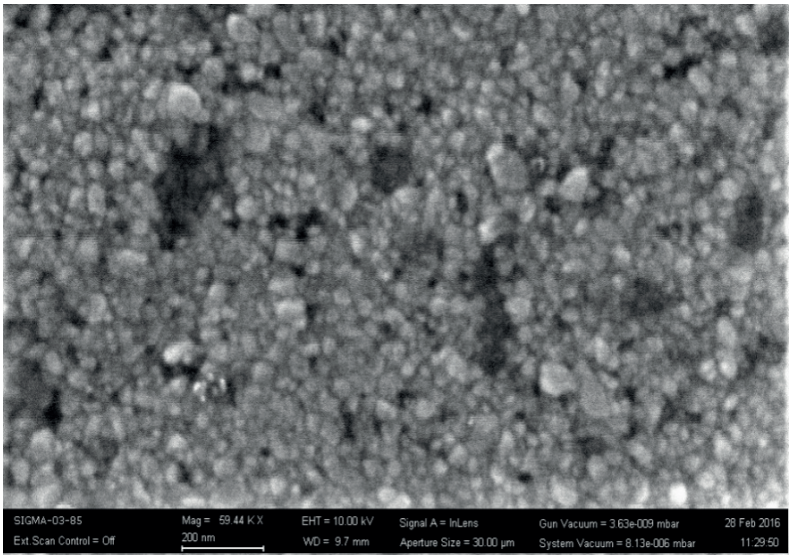

Fig. 4: SEM image of granular Authin film surface with nanoholes and nanocracks.

DISCUSSION

Experimental observation of the Cr/Au thin metal film on PDMS shows that the deposited metal film is filled with granular Au islands occupied with nanoholes and nanogaps. These NanoRacks and nanoholes lead to the high sheet resistance of the metal film compared to bulk metal. Introducing MPTMS molecular adhesive layer in-between the PDMS and Cr/Au film enhances the adhesion between them, which leads to superior film quality.

The surface analysis of the Cr/Au thin film over PDMS film exposed the effect on buckling surface due to the heat treatment on the patterned thin film. Heating the patterned sample demonstrates a simple buckle manipulation technique of thin metal film on soft elastomer without using any prestrain film or ridge guided surface. Figure 5 shows arrays of Au thin film microelectrodes fabricated on a PDMS film for impedance measurement and is useful in biomedical and robotics skin applications. To increase the flexibility of the device, the connecting line is curvedly designed.

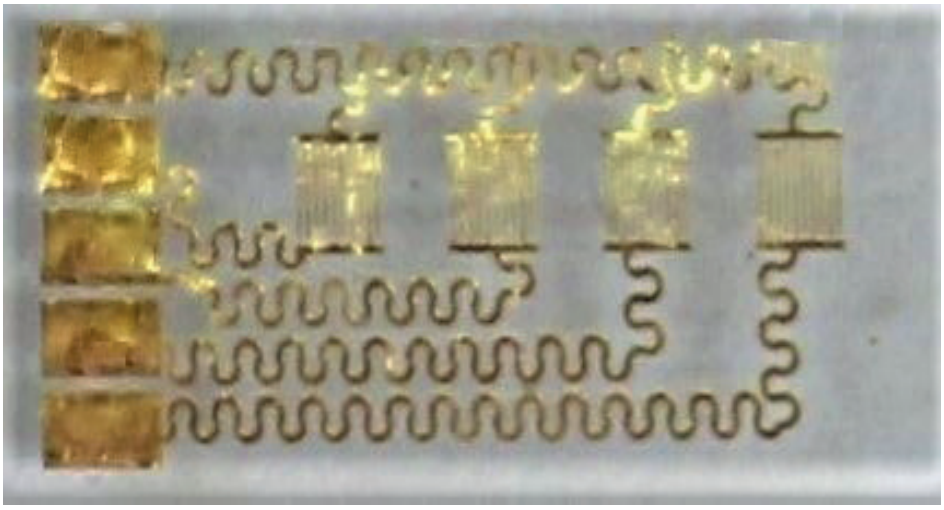

Fig. 5: Photograph of a flexible circuit with arrays of Au thin film microelectrode and curved connecting lines on PDMS substrate for dielectric property measurement.

CONCLUSIONS

The research work presents the fabrication and characterization of the metallic gold thin film micropattern deposited over PDMS elastomeric film for flexible electronic sensor and circuit applications. It is observed that the deposition of self-assembled MPTMS molecular adhesive over the PDMS surface increases the adhesion between a thin metalfilmwithPDMS film. The contact angle measurement of the water droplet placed on the MPTMS layer coated PDMS surface indicates that the hydrophilicity of the modified PDMS surface significantly increases and lasts for an extended period compared to O_2 plasma-treated PDMS surface. Subsequently, the Au thin film was sputtered on bare PDMS, O_2 treated PDMS, and MPTMS molecular adhesive layer coated PDMS with the same deposition conditions using dc magnetron sputtering. Macroscopic adhesion study using a double tape peel-up test confirmed that the deposition of the molecular adhesive layer over the PDMS substrate showed better adhesion with the sputtered Au film compared to the other two PDMS samples. The deposited Cr/Au film was efficiently patterned for microstructure on the PDMS substrate using traditional photolithography and wet etching process, unlike the shadow mask technique that is mostly used for Au thin film deposition on elastomeric PDMS. The stronger adhesion between the thin metal film with the PDMS makes direct patterning using photolithography techniques possible. The random buckles formed on the Au metal film were successively manipulated. The SEM micrograph confirms the Au thin film on the PDMS film is granular and led to the high sheet resistance of the thin metal film. The research is beneficial for the reliable fabrication of sensors and circuits with anAu thin film on elastomeric PDMS film.

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