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Conformable Skin-Like Conductive Thin Films with AgNWs Strips for Flexible Electronic Devices

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Abstract: Keeping good conductivity at high stretching strain is one of the main requirements for the fabrication of flexible electronic devices. The elastic nature of siloxane-based elastomers enables many innovative designs in wearable sensor devices and non-invasive insertion instruments, including skin-like tactile sensors. Over the last few years, polydimethylsiloxane (PDMS) thin films have been widely used as the substrates in the fabrication of flexible electronic devices due to their good elasticity and outstanding biocompatibility. However, these kind of thin films usually suffer poor resistance to tearing and insufficient compliance to curved surfaces, which limits their applications. Currently no three-dimensionally mountable tactile sensor arrays have been reported commercially available. In this work, we developed a kind of mechanically compliant skin-like conductive thin film by patterning silver nano wire traces in strip-style on Dragon Skin® (DS) substrates instead of PDMS. High cross-link quality was achieved then. To further improve the conductivity, a thin gold layer was coated onto the silver nanowires (AgNWs) strips. Four different gold deposition routines have been designed and investigated by using different E-beam and spin coating processing methods. Owning to the intrinsically outstanding physical property of the Dragon Skin material and the uniform embedment built in the gold deposition processes, the DS/AgNWs thin films showed convincible advantages over PDMS/AgNWs thin films in both mechanical capability and conductive stability. Through experimental tests, the DS/AgNWs electrode thin films were proven to be able to maintain high conductivity following repeated linear deformations. *Copyright © 2015 IFSA Publishing, S. L.*

Keywords: Flexible electronic devices, Stretchability, Conductivity, Dragon Skin, AgNWs.

1. Introduction

Imitating human sense by electronic methods is a popular topic in past few years, plenty of research works about flexible electronic devices have been done for this. Artificial sensors with human like sensory capability are one of these devices and will bring in large amounts of heightened artificial intelligence. For example, endowing robots with tactile sensors may greatly extend their application range to some interactive tasks like caring for kids and elders; applying skin-like sensors on embedded medical devices will provide an unprecedented level of diagnostic and detection capability. Compared to the sense of heat [1], light [2], sound [3] and taste [4], the sense of touch is more difficult to mimic, since it requires a kind of relatively large-sized, high spatial resolution, high sensitivity, and fast response tactile sensing array [5], while any of these prerequisites has yet to be fulfilled. Tactile sensors should have the property to accommodate movements while keep their sensing functionalities [6], which requires at least 30 % stretchability [7]. Among various potential solutions, one promising strategy is to make artificial skin with intrinsic flexible, biocompatible substrate and stretchable conductors [8]. There are quite a few candidates for stretchable conductors. Conducting polymers used to be one of the most popular options, however, the lack of simple methods to obtain low cost conductive polymer make them unfavorable afterwards [9]; carbon nanotube [10] and graphene films [11] have high intrinsic conductivity and can be produced with low cost, but they suffered from large tube to tube junction resistance [12]. Most recent studies showed that electrode based AgNWs is one of the most suitable conductors for flexible sensor structures as the interpenetrating networks of AgNWs fits the crosslinked polymer substrates very well [13]. Hu, *et al*., demonstrated AgNW/polymer matrix electrodes, however they only get a small increase of sheet resistance after multiple times of stretches [14]. For the flexible substrates, currently polydimethylsiloxane (PDMS) is undoubtedly the most favorable choice in deformable sensor fabrication, owing to its good biocompatibility, flexibility and good processability, most kinds of conductors mentioned above can be embedded in PDMS structure and work in mechanically deformable forms [15-16]. However, versatility as it is, PDMS based sensors are not complaint enough to mount on three dimension curved surfaces or deforming cylindrical surfaces. Yang, *et al*., designed a highly twistable 8×8 sensor with PDMS substrate and it showed better three-dimensional stretchability than any other PDMS based sensors [17], but the structure is a little too thick to be implemented on diagnostic medical equipment, and the uniformity of the sensing elements is deteriorated after a few twists. Basically, it's proved that PDMS substrate can provide sufficient planer stretchability [18-19], but it's not good enough to work for fully conformable requirements owing to its considerable rigidity and low toughness [20]. In this case, components with higher intrinsic flexibility should be developed and investigated to further enhance the sustainable capability of the conductive layer's of a flexible electrical devices [21].

In our current research, a high performance silicone rubber, named Dragon Skin (DS) by Smooth-On Inc$^{®}$, was firstly used as the substrate to fabricate stretchable electrode thin films. The conductivity was achieved through patterning AgNWs in strip-style on the DS substrates. For stretchability comparison, both PDMS/AgNWs thin films and Dragon Skin/AgNWs thin films have been fabricated. To further improve their conductivity, two types of Physical Vapor Deposition (PVD) processes, sputtering and electronic beam evaporation, were applied to coat a gold layer on the electrode strips. In addition, the adhesion effects of different interlayers (Titanium and Chrome) between the gold trace layer and the AgNWs surface were studied as well. Once assembled, the DS/AgNWs electrode thin films would be subjected to fatigue testing, to further evaluate their ability to perform well in real applications.

2. Fabrication

The following steps have been used to fabricate the proposed PDMS/AgNWs and the DS/AgNWs stretchable electrode thin films:

Step #1: Some liquid PDMS (Dow Corning Sylgard 184, ratio of base to cross-linker is 10:1 by mass) was dispersed on 5 inch silicon wafers by spin coating (spin parameters are shown in Table 1), and was thermally cured in an oven at 65 °C for 12 hours to make molds for AgNWs networks of the electrodes.

Table 1. Parameters for spin coating in Steps #1 and #4.

Process Steps	Parameters		
	Acceleration	Speed	Time
Spread	200 rpm/s	800 rpm	10 s
Spin	250 rpm/s	1000 rpm	30 s

Step #2: AgNWs (Blue Nano, 10 mg/ml) were dried in these PDMS mold on the silicon wafers by a syringe, forming the eight parallel strips of AgNWs networks (Fig. 1a).

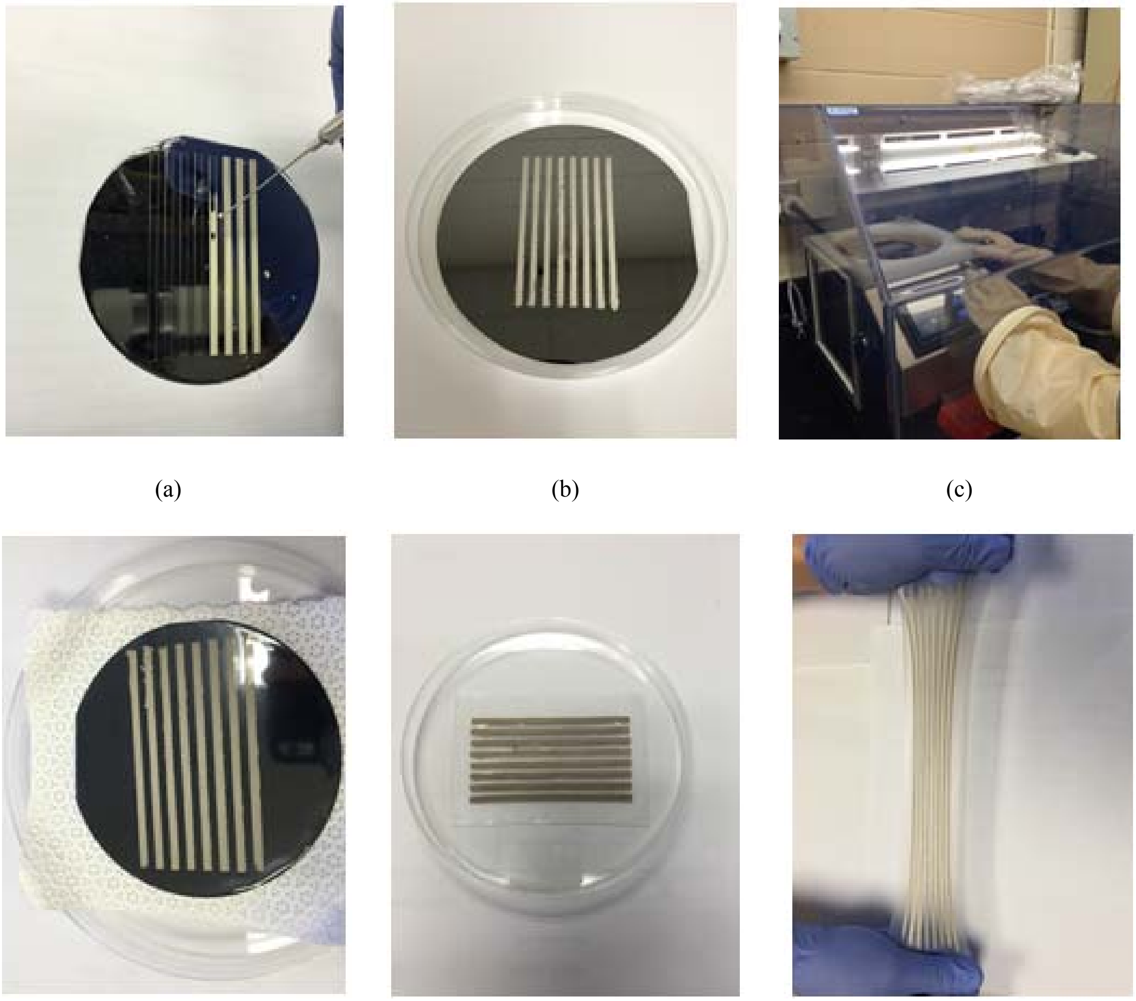
Step #3: As the AgNWs dried, the PDMS mold was removed (Fig. 1b) and the remaining AgNWs strips are patterned.

Step #4: Some liquid PDMS was mixed, degassed and poured over the AgNWs strips, and dispersed by spin coating again (Fig. 1d). The same procedure was repeated when we made the thin films with Dragon Skin as the substrates.

Step #5: Finally, the whole structure was thermally cured for 12 hours, after this, the PDMS (Dragon Skin) electrode thin film was peeled off from the silicon wafer carefully (Fig. 1e).

3. Resistance Measurement and Stretchability Comparison

Following the fabrication process, the stretchable electrode thin films were catogized into 4 groups for further metallization.



(a) (b) (c)

(d) (e) (f)

Fig. 1. (a) Patterning AgNWs conductive strips in a removable PDMS mold; (b) The parallel patterned AgNWs strips; (c) Mixed PDMS (or DS) dispersed on AgNWs by spin coating in a glove box; (d) Thin and uniform electrode thin film after spin coating; (e) The electrode thin film was peeled off from a silicon wafer; (f) The DS based electrode thin film can be stretched over 150 %.

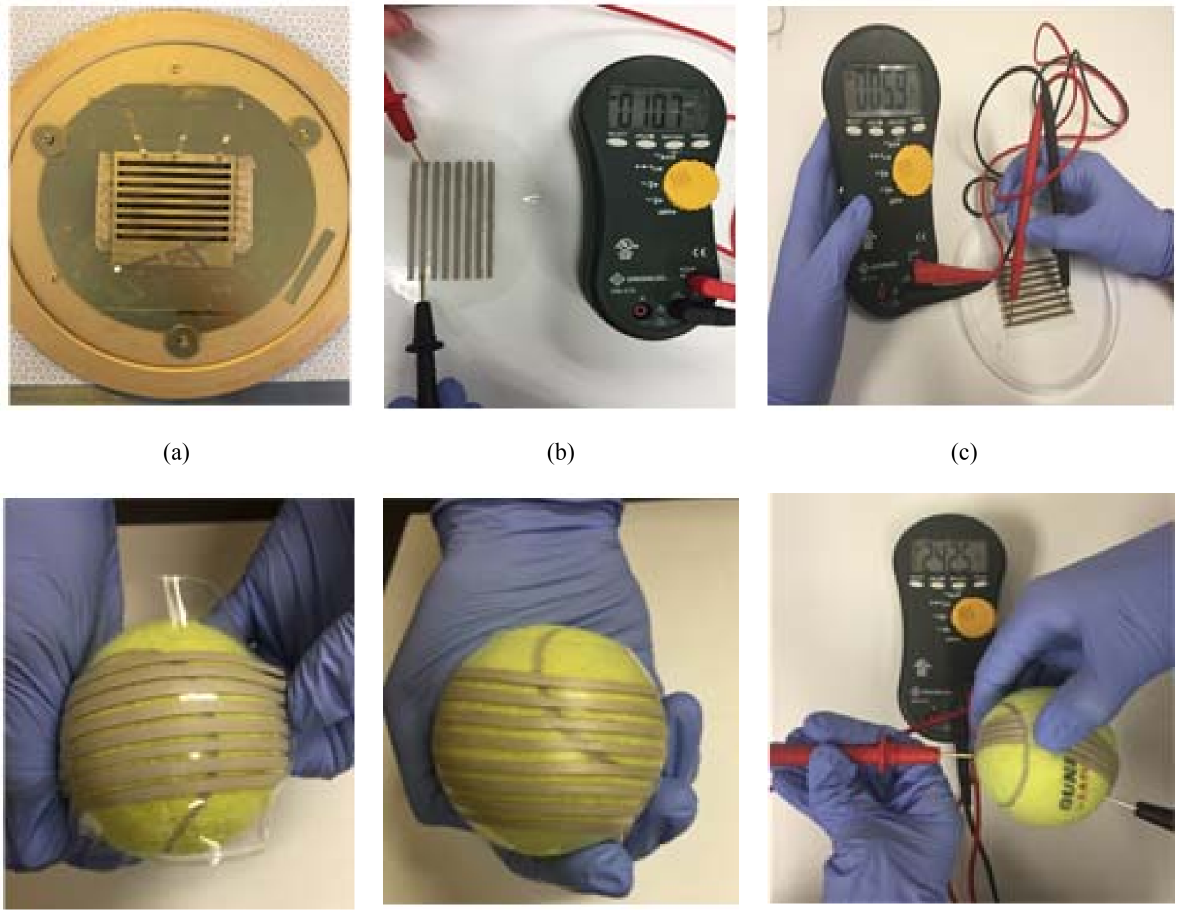
A sputtering system from AJA International, Inc. and an evaporation system from CHA Industries, Inc. were utilized to coat a thin gold layer on different groups of the AgNWs conducting strips. Titanium (Ti) and chrome (Cr) were applied as the adhesion layer for the deposition of gold layer respectively. Ti and Cr have been commonly used in assembling different kinds of metal powders with silicon-rubber thin films to form a multilayer structure in electrical contact relays, as an adhesion/diffusion media [22-23]. They can also introduce considerably adhesion improvement for gold powers. The applied parameters in our process are shown in Table 2.

A 10 nm interlayer was achieved in each of the sample groups, and a 50 nm gold layer was coated in succession as shown in Fig. 2a. The measurements for stretchable electrodes were shown in Fig. 2b and Fig. 2c. Resistances of each group are listed in Table 3. At least 16 different conducting strips have been measured for each PVD process to get the reliable values.

From the data shown in Table 3, it's noted that the resistance of group #2 strips, which were coated with a 50 nm gold thin layer with chrome as interlayer by E-beam, is the smallest among all the strips with and without PVD processing.

Table 2. Parameters for different PVD processes.

No.	PVD Process	Metalized layer	Parameters		
			Chamber Pressure	Depo-sition Rate	Total Time
#1	E-beam evaporation	Ti(10 nm)+ Au(50 nm)	1.5×10^{-6} Tor	0.2 nm/s	300 s
#2		Cr(10 nm)+ Au(50 nm)			
#3	Sputtering	Ti(10 nm)+ Au(50 nm)	1.0×10^{-5} Tor	0.25 nm/s	240 s
#4		Cr(10 nm)+ Au(50 nm)			



(a) (b) (c)

(d) (e) (f)

Fig. 2. (a) Stretchable electrodes flipped under a mask on a sample holder for PVD processes; (b) Resistance of a 60 mm AgNWs conducting strip is about 11 Ω; (c) Resistance of a 80 mm AgNWs/Cr/Au (E-beam deposited) conducting strip is below 6 Ω; (d) A tennis ball is wrapped by an AgNWs/PDMS electrode thin film; (e) A tennis ball is tightly wrapped by an AgNWs/DS electrode thin film; (f) The AgNWs/DS electrode thin film can keep low resistance under large 3D deformation.

Table 3. Resistances of the stretchable electrodes after different metallization routines.

No.	Conductor Strip	Resistance (Ω/1mm)
#0	AgNWs	0.178
#1	AgNWs/Ti/Au by E-beam	0.125
#2	AgNWs/Cr/Au by E-beam	0.084
#3	AgNWs/Ti/Au by sputtering	0.157
#4	AgNWs/Cr/Au by sputtering	0.103

There are mainly two reasons explaining this. One is that the chrome has higher inter-diffusion rate with AgNWs, and provides better adhesion force for the AgNWs to contact with each other in these samples.

Another reason is that the E-beam evaporation permits more direct energy transfer to the source during heating than sputtering; due to the higher vacuum degree achieved, the E-beam can get purer evaporated material to the substrate, thus the electrode processed by E-beam shows better conductivity than those by sputtering.

From Fig. 2d and Fig. 2e, it is also observed that although the PDMS-based electrode substrate is thin, it could not be conformably mounted to a curved surface and the two sides of the PDMS/AgNWs thin film tilt up on the tennis ball, while the DS-based electrode thin film could be wrapped around a tennis ball tightly and conformably. In Fig. 2f, a 80 mm long AgNWs/DS electrode thin film can be wrapped around a tennis ball (r = 33 mm) with elongation of nearly 160 % and still keep a resistance of 2.2 Ω/1 mm, which is on the top level of any kinds of stretchable electrodes under large deformation.

4. Fatigue Test

In the actual application, the stretchable thin films with conductive strips will be used in a working condition with repeated stretching and relaxing motions. Thus fatigue the property of this kind of thin films is one of the important factors which will influence its applicability. In the following, the tests to demonstrate the capability of the thin films to withstand repeated deformation were carried out. Its conductivity after the repeated motion was measured to evaluate its anti-fatigue property.

The experimental setup is shown in Fig. 3. The main testing component is a piece of DS/AgNWs thin film with 8 conductive strips. One side of the thin film was clamped to the end-effector of an EPSON robot and the other side was fixed to the table using a table mounted clamp. The end-effector of the robot was then controlled to move repeatedly to generate repeated stretching and relaxing motion.

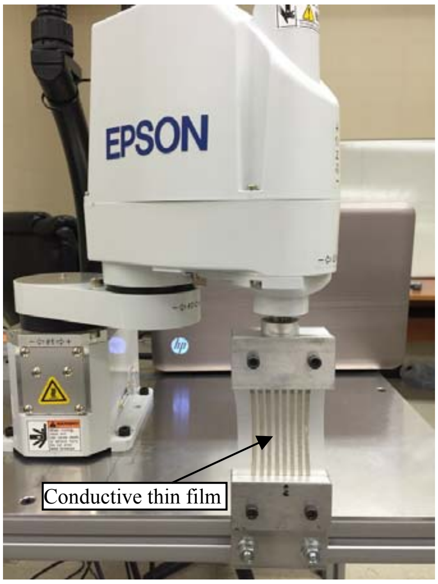


Fig. 3. Fatigue test setup.

After the DS/AgNWs electrode thin film was stretched and relaxed for certain times, such as 1 time, 3 times, 5 times and 100 times, it was taken off from the robot and mounted to a tensile testing stage for measurements as shown in Fig. 4. On this stage, the resistances of the conductive strips on the thin film were measured at certain strain rates from 0 % to 70 %, such as 5 %, 10 %, 15 %, etc. The results measured in resistances per mm were shown in Fig. 5.

From results shown in Fig. 5, a linear relationship between the increase of the resistance per millimeter and the increase of the strain rate can be observed. It can also be observed that the more times the thin film was stretched, the bigger the thin film's resistance was. There was an average overall of 12.5 % increase in resistance from the first to third stretching, 14.9 % increase after the 5th stretching, and 24.8 % following the 100th stretching. After around 100 times stretching, the resistance of the thin film did not increase any more. This is to say that the DS/AgNWs electrodes can withstand repeated stretching and maintain high conductivity when working in a reasonable range of strain (0 % - 70 %).

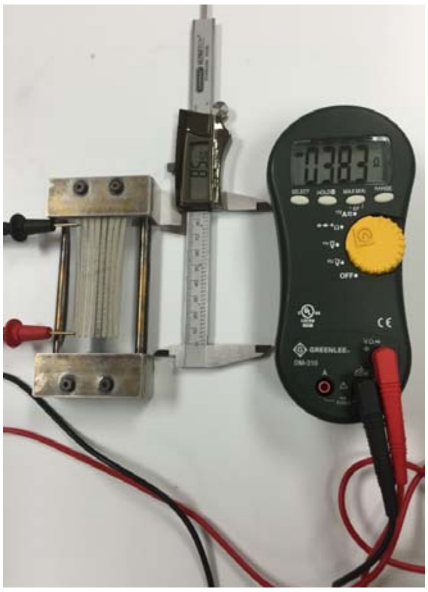


Fig. 4. Resistance measured under different strain rates using a tensile testing stage.

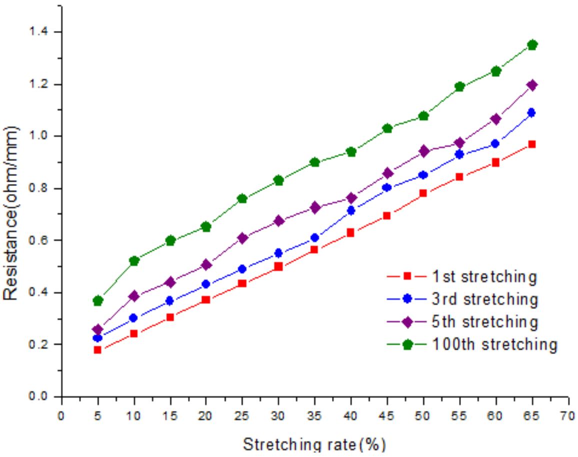


Fig. 5. Resistance of an AgNW/Dragon Skin stretchable conductive strip as a function of tensile strain at different stretching cycles.

5. Conclusions

Flexible thin films with high conductivity and good stretchability will facilitate the design and fabrication of flexible electronic devices, such as skin-like sensors. In this paper, a new type of high stretchable silicone, Dragon Skin, together with AgNWs has been used to fabricate conducting electrode thin films. The thin films with the electrode strips have showed better conformability to curved surfaces and higher capability to withstand large 3D deformation than the commonly used PDMS flexible electrode thin films. To further study the conductivity of the stretchable electrodes, a comparison of different surface deposition routines was conducted, i.e. gold powder deposition using E-beam deposition and spin coating methods. The results indicate that by coating a thin gold film with chrome as interlayer by electronic-beam evaporation, the DS/AgNWs electrode thin films can achieve better conductivity under stretching than those with or without surface depositions. Fatigue tests were also carried out on the DS/AgNWs electrode thin films. It was found that the repeated deformations caused limited increases in the electrode resistance. This makes the Dragon Skin/AgNWs electrode thin films a promising component for flexible electronic devices.

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