Thin Solid Films 519 (2011) 5511–5515

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Electromechanical stability of buckled thin metal films on elastomer

Donyoung Kim, Hyun-Sik Hwang, Dahl-Young Khang *

Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Republic of Korea

ARTICLE INFO

Article history:
Received 13 October 2010
Received in revised form 8 March 2011
Accepted 16 March 2011
Available online 31 March 2011

Keywords:
Buckling
Metal thin films
Stretchable electronics
Oxidation
Electrical resistance
Capping layer

ABSTRACT

Oxidizable metals such as Al are found to become highly resistive when exposed to air in buckled state, >10× resistance increase compared to that in flat configuration. On the other hand, noble metal and oxide conductor films, such as Au and indium tin oxide show negligible resistance increase. The enhanced oxidation of grain boundaries that are exposed to air when buckled is found to be responsible for the observed electromechanical stability. Simple yet effective method, i.e., thin capping layer of noble metal, to prevent the oxidation of non-noble metal is proposed and experimentally verified.

1. Introduction

As an emerging field, stretchable electronics has attracted many scientific and practical interests in recent years [1–11]. Thanks to its electrical/electronic stability under mechanical deformation, i.e., electromechanical stability, stretchable electronics may find wide applications such as bio-implantable devices, wearable electronics, and other fascinating future electronics. For the success of those envisaged applications, however, stretchable interconnection should be made possible concomitantly. Electrical interconnection among devices, as well as devices and the outside world, is an essential ingredient for the whole system to be stretchable. Furthermore, the stretchable interconnection becomes utmost important in implementing "hybrid" stretchable electronics, where the rigid device islands (typically finished on other substrates) are assembled on a stretchable substrate [12,13]. In this approach, the main remaining part for the stretchable electronics lies in the electrical interconnection among device islands, which must be stretchable to make the whole assembly stretchable. Gray et al. [14] and other research groups [15–17] have fabricated two-dimensionally serpentine flat metal films that are embedded into elastomer to make them electrically conducting even when mechanical strain is applied. Another interesting approach is to use buckled wavy metal thin film on elastomeric substrate [18–23].

Due to its ductile and noble (non-oxidizable) properties, gold (Au) has been used exclusively in most of previous works, both in embedded serpentine and in buckled wavy film approaches. In real situations, however, various kinds of metals other than Au are required for a given specific application. In most electronic device applications, the relative arrangement between work function of the metal and conduction/valence bands of semiconductor materials in energy diagram plays a critical role in determining device performance. For example, aluminum (Al) is the electrode material of choice for electron extraction in bulk heterojunction (BHJ) organic solar cells due to its high work function [24] while calcium (Ca) is the one for hole injecting electrode in organic light emitting diodes (OLEDs) due to its low work function [25]. These non-noble metals are prone to form native oxide on their surfaces when exposed to air. Furthermore, the oxidation may not be limited to thin surface region of metal when the film takes the wavy profile induced by buckling, due to the grained microstructure of and micro/nano scale cracks in those metal films, which may eventually result in non-conducting or highly resistive metal. In fact, we tried to fabricate stretchable BHJ organic solar cells on elastomer using Al as an electron-extracting electrode and found that evaporated thin (<100 nm) Al films became almost non-conducting in buckled state. In this letter, we show that the observed resistance increase is due to the oxidation of metal grains exposed to air by buckling. Also, this electromechanical stability problem is shown to be prevented simply by adding capping layer of noble metal on top of non-noble ones.

2. Experimental details

Polydimethylsiloxane (PDMS), Sylgard 184 (Dow, USA), was used as an elastomeric substrate. Base resin and curing agent were mixed in a 10:1 weight ratio, degassed, poured in petri-dish, and then cured for

* Corresponding author at: Department of Materials Science and Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, Republic of Korea. Tel.: +82 2 2123 5835; fax: +82 2 312 5375.
E-mail address: dykhang@yonsei.ac.kr (D.-Y. Khang).

0040-6090/$ – see front matter
doi:10.1016/j.tsf.2011.03.042

12 h in convection oven at 60 °C. The cured PDMS was cut into rectangular shape (20 mm 50 mm) by razor blade, and stretched (3–10%) one-dimensionally by custom-built stretching stage during metal deposition. Releasing the prestrain of PDMS after the deposition makes the metal film buckled. Sputtering (Au, indium tin oxide) or e-beam evaporation (Al) was used for thin metal film preparation with shadow mask. The shadow mask has opening of 0.1 mm 15 mm (width length), with large (3 mm 3 mm) contact pads at both ends. Electrical resistance was calculated from the slope of current–voltage curve measured by semiconductor analyzer (HP 4156B), and normalized to that of zero strain (i.e., initial buckled state).

For mock-up experiment, steel balls with diameter of 400 μm are stacked and embedded in PDMS. The embedding PDMS was prepared and cured by same methods and conditions as mentioned above. A slab of PDMS with embedded steel balls was stretched and compressed one-dimensionally by custom-built stretching stage during optical microscope analysis.

3. Results and discussion

When the metal/PDMS sample is released from the prestrain that was applied during metal deposition, the surface takes a wavy configuration. The applied compressive strain is relieved by this buckling process, as shown in top panel of Fig. 1(a). When the Au/PDMS sample was stretched to at/around prestrain value that was applied during the deposition, the film took almost flat configuration. The film took another wavy shape (sinusoidal waves perpendicular to the applied stretching strain direction), as shown in the bottom panel of Fig. 1(a), due to Poisson effect, when the stretching strain slightly exceeded the value at which the film takes almost flat shape. The film started to have cracks and eventually was ruptured upon applying much larger tension than the prestrain value. The electrical resistance of the metal film was measured while applying different degree of tension, from zero strain (i.e., initial wavy state) to slightly above the prestrain value.

The overall shape of the resistance curve, shown in Fig. 1(b), shows asymmetric parabola; that is, there exists a minimum in resistance value at tensile strain at/around the prestrain value applied during deposition. At/around those minima, the film is in flat and unstrained state. On the left part of those minima, the films are in buckled wavy state, and shows slow decrease in electrical resistance as a function of applied tensile strain. On the other hand, the films are under pure tension on the right side of the minima and shows rather steep increase in resistance. The increase of resistance under pure tension follows the quadratic [26,27] dependence on the applied strain, $R \propto \varepsilon^2$. And the resistance change as a function of applied strain was fully reversible for the Au/PDMS samples, in agreement with previous literatures [19–23], unless the applied strain exceeds a value at which the films break.

The change in electrical resistance is originated from the microstructural change in metal layer occurring during external loading. As shown in Fig. 2 schematically, external tension (compression) increases (decreases) the gap distance between metal grains, leading to change in the number of electrically conducting percolative paths. At the peaks of buckled state, the enlarged nanoscale gaps between grains make the film more resistive. As the external strain is increased to prestrain value, the film takes the flat configuration as it does during deposition and heals the nanogaps, leading to more percolation paths. In addition to these nanoscale gaps, micro/nano scale cracks may play the similar role. This hypothesis explains well the experimental results (Fig. 1(b)), in which there exists a minimum in resistance versus strain curve at/around prestrain value.

A mock-up experiment with stacked steel balls embedded in PDMS supports this hypothesis, as shown in Fig. 3. The change in spacing (i.e., center-to-center distance) of the steel balls was measured as a function of applied strain, based on optical microscopy image. As shown in Fig. 3(b), the spacing increases upon applying tensile strain, while it decreases upon compression. The same event is supposed to occur in metal layer on PDMS when buckled. At the wave peaks, nanoscale gaps would occur and this leads to decrease in the number of percolative conducting paths.

While buckled Au thin film shows electromechanical reversibility [23] due to its non-reactive, inert nature to ambient air, the nanoscale gaps between metal grains in the buckled state may be problematic for non-noble metals: the enhanced oxidation of the exposed grain boundaries can lead to *irreversible* change in conductivity. Once the grain boundaries are oxidized, then the film becomes highly resistive even when the film gets back to flat state. To check this possibility, we performed the same experiments with Al, which is well-known to form native oxide on its surface when exposed to room ambient.

In the case of the buckled Al film, as expected, it became highly resistive irreversibly once the sample took buckled shape and remained at room ambient in a minute, for Al films thinner than ~200 nm. Even for thicker Al film (300 nm) on PDMS, as shown in Fig. 4, it becomes highly resistive (~1000× increase in electrical resistance) in a week. This is the direct evidence of increased oxidation around exposed grain boundaries at the peaks of sinusoidally buckled surface, which leads to the increased electrical

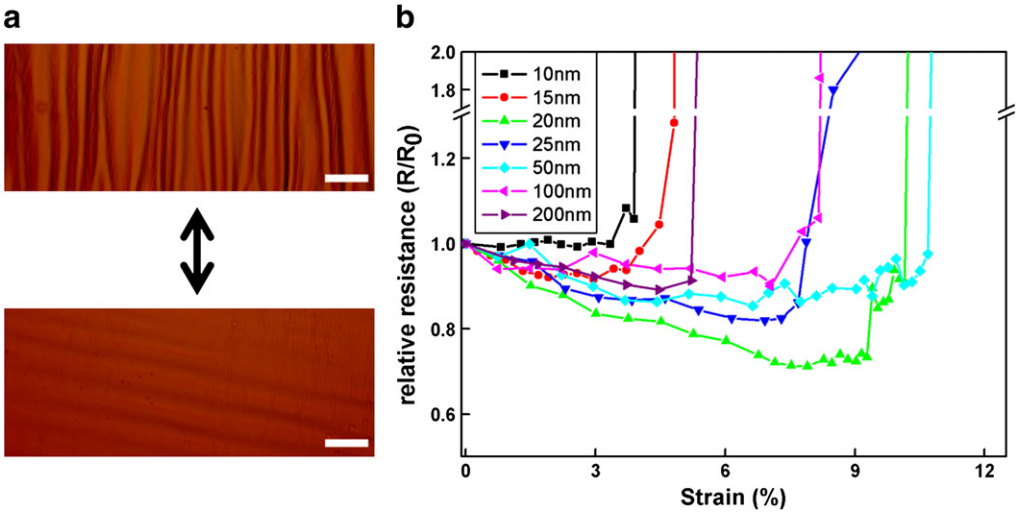

Fig. 1. (a) Optical micrograph images of buckled Au (200 nm) film on PDMS substrate. (top) Initial wavy state with 6% of prestrain, (bottom) stretched up to 7% of strain, which is slightly higher value than the prestrain. Scale bars indicate 20 μm in both images. (b) The change of electrical resistance of buckled Au films as a function of external stretching.