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Oxygen Plasma를 이용한 Poly(dimethylsiloxane) 기판 상에 증착된 은 전극의 변형 능력 향상

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Improvement of the Stretching Capability of a Silver Electrode on a Poly(dimethylsiloxane) Substrate by Oxygen Plasma

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초록: 본 연구에서는 산소 플라즈마 처리된 poly(dimethylsiloxane)(PDMS) 기판 위에 은 전극을 사용하여 신축성 있는 전극을 제작하였다. 신축성있는 기판 상에 은 전극을 직접 증착함으로써 복잡한 전사과정을 피할 수 있다. 간단한 산소 플라즈마 처리를 통해 신축성 기판표면에 탄소 불순물을 줄이고 은 전극과 신축성 기판 사이의 접착력을 강화할 수 있어서, temporal 및 prolonged mechanical strain 측정 시, 전극의 신축 능력과 안정성을 향상시킬 수 있었다.

Abstract: In this study, stretchable electrodes are demonstrated with silver electrodes on an oxygen-plasma-treated poly(dimethylsiloxane) (PDMS) substrate. The direct deposition of a silver electrode on a compliant substrate was used to avoid a complicated transfer process. We found that the stretching capability and stability under temporal and prolonged mechanical strain are improved by a simple oxygen plasma treatment on the compliant substrate due to the modified surface with reduced carbon impurities and enhanced adhesion properties between the Ag and the compliant substrate. The results show that the oxygen plasma treatment is useful for forming highly stable metal electrodes on a compliant substrate because it minimizes the number of processing steps needed.

Keywords: poly(dimethylsiloxane), silver electrode, stretchable electrode.

Introduction

Recently, stretchable electrodes on a compliant substrate have been widely investigated for flexible, rollable, and stretchable electronic applications.[1-3] Among the various stretchable electrode materials, metal electrodes are considered as the most important stretchable electrodes candidates owing to the simple fabrication process and high conductivity.[4,5] It has been reported that stretchable electrodes can be fabricated on compliant elastomeric substrates using gold/titanium and silver metal materials.[5,6] Silver is the most adequate metal for the stretchable electrode because it has the highest conductivity among various metals. Most previous reports used a transfer method to transfer the metal electrodes from a sacrificial layer to a compliant substrate.[5] However, the transfer method is relatively complicated if used to form a stretchable electrode, as an additional wet etching process of a sacrificial layer is always required. The direct deposition of the electrode on the compliant substrate is a simple and cost-effective means of fabricating a stretchable electrode structure. In this case, a small variation of the resistance not only under temporal strain but under prolonged mechanical stress is required for stable operation of the stretchable electrodes. Unfortunately, the performance of the stretchable electrode is poor when the metal electrodes are directly deposited on the poly(dimethylsiloxane) (PDMS) substrate. To improve the stretching capability, an additional treatment is required for the application of the direct deposition method.

Here, we demonstrate stable stretchable silver electrodes on

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a compliant PDMS substrate. We found that a simple oxygen plasma process on the PDMS substrate can effectively improve the stability under a temporal and prolonged stress condition. The underlying physics of the improvement is analyzed based on the crack evolution of the metal electrode.

Experimental

Compliant substrates were prepared using PDMS (Sylgard-184, Dow Corning Inc.). A base polymer was mixed with a cross-linker at a weight ratio of 10:1. The mixture was then poured onto a mask substrate and baked on a hot plate at 150 °C for 10 min. Two samples were prepared before the deposition of the silver electrode. One sample is a reference sample without any surface treatment. The other sample was prepared by an oxygen plasma treatment on the PDMS surface (plasma sample) under the process conditions of 80 W (power), 1.4 torr (pressure) and 80 sccm (flow rate) for 15 sec. The plasma treatment power and time was optimized to minimize the plasma damage of the PDMS surface. We performed the plasma treatment under three different conditions according to plasma power and time with the same pressure and flow rate (condition 1: 20 W, 30 s, condition 2: 40 W, 30 s, condition 3: 80 W, 15 s). The best performance of the stretchable electrode was obtained in condition 3. We found that plasma time is dominant factor to obtain the best performance of the plasma treated samples. The condition 3 is used to analyze the plasma effect on the stretchable electrode. The prepared compliant substrates were fixed on the sample zig under a shadow mask. Then, fifty-nanometer-thick silver electrodes were deposited using a thermal evaporator. The length and width of the electrodes were 2 and 0.4 cm, respectively. Two-point measurements of the resistance were conducted using an Agilent 34450A device under a stretching condition. We measured the variation of the electrical characteristics under both temporal strain (one-cycle) and prolonged strain (multiple-cycle).

Results and Discussion

Figure 1 shows the variation of the sheet resistance for the reference and plasma samples after one-cycle strain. The inset in Figure 1 is an image of an Ag electrode on a PDMS substrate. The electrodes were stretched up to 20% and then released down to the initial length with a stretching speed of 0.2 mm/s. Both samples show increases of the sheet resistance as the strain increases. However, the plasma sample shows relatively low minimum (as deposited, 1.59 Ω/□) and maximum sheet resistance (at maximum strain, 6.73 Ω/□) compared to those of the reference sample (minimum: 2.15 Ω/□ and maximum: 9.97 Ω/□). The improvement of the minimum and maximum resistance of the plasma sample revealed that the quality of the Ag metal on the PDMS substrate is improved after the oxygen plasma treatment. It should be noted though the unoptimized sample of the plasma treatment condition shows good initial sheet resistance (as deposited, 0.8 Ω/□), it shows bad stretching capability in comparison with the plasma sample. This is possibly due to surface damage during the plasma treatment process. Accordingly, the optimization of the plasma process is important to obtain the best performance of the stretchable electrode. Then, multiple-cycle strain, typically used in fatigue tests, is applied to the Ag metal electrode.[6] Figure 2 shows the resulting sheet resistance variations of the reference and plasma samples under multiple-cycle strain up to 499 times with a stretching speed of 0.5 mm/s. It can be seen that there are gradual increases in the sheet resistance for both the reference and plasma samples. However, steeper increases in the minimum and maximum resistance were observed for the reference sample. After 499 cycles, the maximum and minimum resistances of the plasma sample were approximately 2.3 times lower than those of the reference sample. This reveals that the plasma sample shows much more stable operation under the multi-cycle strain condition compared to one-cycle strain condition because the maximum and minimum resistances of the plasma sample are only 1.4 times lower than those of the reference sample for the one-cycle strain condition.

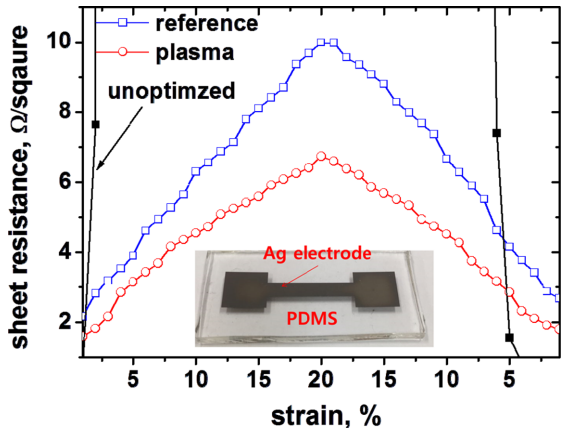

Figure 1. Sheet resistance *vs*. the strain graph for the plasma and reference samples (one-cycle). The black symbol denotes sheet resistance of an unoptimized sample (power: 20 W, time: 30 s). The inset is a photo image of an Ag electrode on a PDMS substrate.

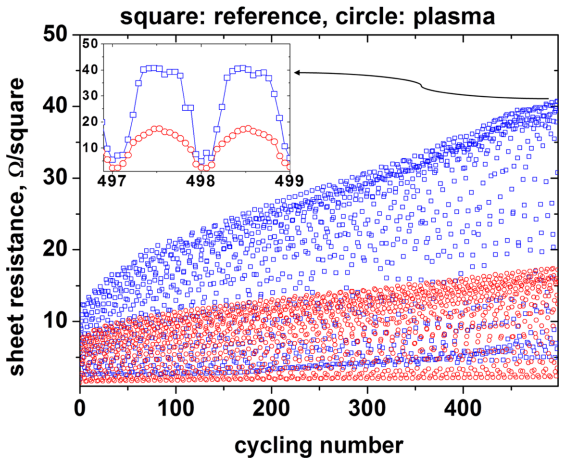

Figure 2. Sheet resistance *vs*. the cycling number graph for plasma and reference samples under multiple-cycle strain. The inset is the graph from the 498th to the 499th cycling results.

The inset of Figure 2 shows the variation of the sheet resistance at the final cycle (the 499th cycle). In the reference sample, a slight decrease of the resistance was observed with an increase of the strain under a large amount of strain. This interesting behavior is observed when many lateral cracks are formed along the stretching direction.[6] When the PDMS substrate is stretched along the length direction, contraction of the substrate along the width direction occurs concurrently leading to a slight decrease of the resistance via the closing of lateral cracks, especially when a large amount of strain is applied. This indicates that a larger number of lateral cracks in the reference sample than those in the plasma samples are generated under the multiple-cycle strain condition.

Figure 3(a) and 3(b) depict optical microscope images of the reference and the plasma samples before multiple-cycle strain, and Figure 3(c) and 3(d) depict the images of the samples after multiple-cycle strain, respectively. After prolonged strain, numerous cracks formed along the lateral and vertical directions of both samples, as shown in Figure 3(c) and 3(d). It should be noted that the repeated contraction of the width direction causes wavy-like stress pattern in the Ag electrodes shown in Figure 3(c) and 3(d). It is known that the Poisson's ratio of the PDMS substrate is about 0.5, which means if the PDMS substrate is stretched by 20% in the length direction, it is contracted by 10% in the width direction. Because the electrode cannot be contracted, the contracted stress along to the width direction makes the wavy-like structure when the PDMS is stretched along to the length direction. This can further degrade the performance of the stretchable electrodes. The number of cracks in the reference sample is much larger than

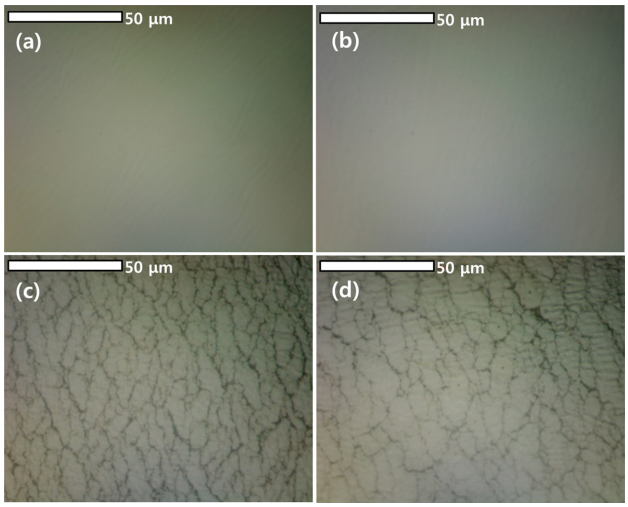

Figure 3. Microscope images of Ag electrodes for (a) the reference (as-deposited); (b) the plasma sample (as-deposited); (c) the reference after 499 multiple-cycle strain cycles; (d) the plasma sample after 499 multiple-cycle strain cycles.

that of the plasma sample because the grain size of the crack-free region of the Ag electrode is much larger than that of the reference sample, which is consistent with the inset of Figure 2. This can be confirmed from the fast Fourier transform (FFT) of the microscope images.

Figure 4(a) and 4(b) show FFT results of Figures 3(c) and 3(d), respectively. The x and y axes denote transformed frequencies of the microscope images. It can be seen that the grain size of reference sample is widely distributed from low to high frequency (high to low period) whereas that of plasma sample is narrowly distributed near the center of the origin (high period). This difference is closely related with the difference of ductility of the Ag electrode on the PDMS substrate. When the ductility is high, there form a small number of cracks because the Ag electrode sustains large strain without disruption. In this case, the grain size of the Ag electrode on the PDMS substrate becomes large as shown in Figures 3(d) and 4(b). Accordingly, it is confirmed that the stretching capability of the Ag electrode of the plasma sample is improved for both temporal and prolonged strain conditions. The origin of such an improvement of the plasma sample is closely related to the surface termination of the PDMS substrate. It is well known that the surface of a pristine PDMS substrate is terminated by -O and -Si$(CH_3)_2$- groups.[7] When an oxygen plasma treatment is applied to the PDMS substrate, an -OH group through a reduction in the methyl (-CH_3) group develops, which enhances the intermolecular strength in the PDMS surface. The formation of -OH group can be confirmed by measuring contact angles

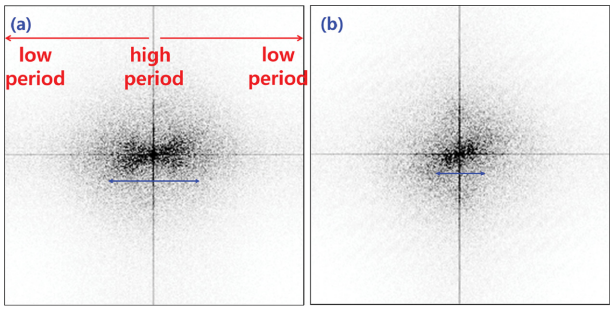

Figure 4. Fast Fourier transform images of (a) the reference; (b) the plamsa sample after 499 multiple-cycle strain.

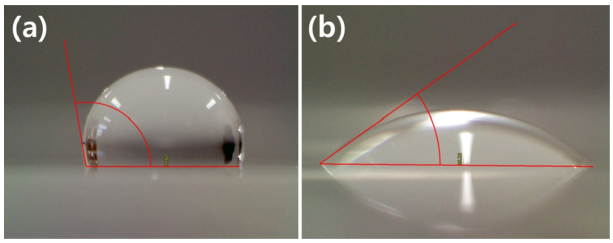

Figure 5. Contact angle of deionized water for (a) reference; (b) plasma samples.

of deionized water. Figure 5(a) and 5(b) show the contact angle results of the reference and plasma samples, respectively. After the plasma treatment, the contact angle was significantly decreased from 99.8 to 36.3°. This clearly reveals that the surface of the PDMS substrate is varied from hydrophobic to hydrophilic states after oxygen plasma treatment. Because the contact angle is the indicator of the formation of the -OH group, we can understand that this leads to improve ductility and resistivity of the Ag metal by increasing the adhesion property. In addition, it is known that the silica-like layer is formed when the plasma treatment is applied to the PDMS substrate. The silica-like layer reduces the effect of carbon impurities of the substrate due to the increment of surface hardness. Because pure metal shows further large ductility compared to contaminated metal, blocking the carbon impurities can enhance the ductility of the Ag electrode on the PDMS substrate.

In summary, there are two major effects of an oxygen plasma treatment: an improvement of the adhesion between the PDMS and the metal, and the removal of carbon impurities, resulting in an improvement of the as-deposited minimum resistance and stretching capability of the stretchable Ag electrode.

Conclusions

The stretching capability of an Ag electrode on an oxygen-plasma-treated sample showed good stretching capability and stability under temporal and prolonged stress conditions. The direct deposition of a metal electrode on a compliant substrate causes many problems because the substrate contains a large number of impurities, which leads to low conductivity and poor adhesion properties. This obstacle is overcome by a simple oxygen plasma treatment. This method can be applied to other metal electrodes such as Au, Cu, and Al. Especially, it is more useful for the metal electrodes which are weak to contamination of the compliant organic substrate (PDMS or other compliant substrate) such as Cu and Al. It is known that the UV-ozone treatment on the PDMS substrate changes hydrophobic to hydrophilic surface with an increase of the surface hardness. However, merits of the plasma treatment are easy control of process parameters in the plasma exposed region and a decrease of process time in comparison with the UV-ozone treatment. Therefore, this method can be used to fabricate high-performance and stable stretchable electrodes with a minimal number of fabrication steps.

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