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Surface treatment of silver-paste electrode by atmospheric-pressure plasma-jet

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대기압 플라즈마 제트를 이용한 실버페이스트 전극의 표면처리

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요 약 : 실버 페이스트는 상대적으로 낮은 열처리로 공정이 가능하기 때문에 전자 소자 응용분야에서 유용한 전극 재료이다. 본 연구에서는 은 페이스트 전극에 대기압 플라즈마 제트를 이용하여 전극 표면을 처리 했다. 이 플라즈마 제트는 11.5 kHz 작동 주파수에서 5.5 ~ 6.5 kV의 고전압을 사용하여 아르곤 분위기에서 생성되었다. 플라즈마 제트는 대기압에서 수행함으로써 인쇄 공정에 더 유용할 수 있다. 플라즈마 처리시간, 인가된 전압, 가스유량에 따라 전극의 표면은 빠르게 친수성화 되었으며 접촉각의 변화가 관찰되었다. 또한, 대면적 샘플에서 플라즈마 처리 후 접촉각의 편차가 없었는데, 이는 기판의 크기에 관계없이 균일한 결과를 얻을 수 있었다는 것을 의미한다. 본 연구의 결과는 대면적 전자소자의 제조 및 향후 응용 분야에서 적층 구조를 형성하는데 매우 유용할 것으로 기대된다.

주제어 : 대기압, 플라즈마 제트, 은(Ag) 페이스트 전극, 표면 처리, 접촉각, 표면 에너지

Abstract : Silver paste is a valuable electrode material for electronic device applications because it is easy to handle with relatively low heat treatment. This study treated the electrode surface using an atmospheric-pressure plasma jet on the silver-paste electrode. This plasma jet was generated in an argon atmosphere using a high voltage of 5.5 to 6.5 kV with an operating frequency of 11.5 kHz. Plasma-jet may be more beneficial to the printing process by performing it at atmospheric pressure. The electrode surface becomes hydrophilic quickly and contact angle variation is observed on the electrode surface as a function of plasma treatment time, applied voltage, and gas flow rate.

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Also, there was no deviation in the contact angle after the plasma treatment in the large-area sample, that means a uniform result could be obtained regardless of the substrate size. The outcomes of this study are expected to be very useful in forming a stacked structure in the manufacture of large-area electronic devices and future applications.

Keywords : Atmospheric pressure, Plasma jet, Silver(Ag) paste electrode, Surface treatment, Contact angle, Surface energy.

1. Introduction

Electrical paste, carbon, graphene, metal nanoparticles, and other conductive materials are currently utilized for various applications as per different requirements[1]. Even gold is an expensive element among these materials and has excellent conductivity, and it cannot be used all the time due to its high cost. However, silver (Ag) is a high-conductivity (electrical and thermal) material. It is additionally inexpensive[1][2] with good chemical stability compared with other materials for high conductive properties and high surface energy[3]. It is beneficial for forming electrodes for many applications due to its properties with the large substrate[4]. According to specifications, Ag was successfully synthesized in numerous forms, including nano silver paste, silver nanoparticles, and conductive ink. Silver materials can also be employed in optoelectronics, transistors, sensors, and other surface energy control applications[5]. Surface energy is required to create a unit of energy that can make a specific sample using a different approach[6].

That can be helpful to the absorption of the liquid molecule on materials to increase hydrophilicity. In recent years, hydrophilicity controlled to develop more surface energy has been observed with various methods as per their practical application[7]. Such practices have dramatically improved the surface properties of the sample. To date, many ways have been established for its surface modification, including ozone treatment, UV treatment, oxygen treatment, and plasma treatment[8-10]. As thermally sensitive substrates can be used to treat, plasma treatment is beneficial in cleaning impurities. Surface modifications were used to develop new linear interpolation using metals, polymers, or glasses[11].

Moreover, plasma treatment enhances the substrate's surface charge, which improves thin film adhesion hole development (Lisco et al., 2014)[12], and it can change surface qualities. Decreasing the time it takes to modify the surface is a primary driving force of surface energy research[13]. It contributes to more surface deployment to solid surfaces with a larger area sample.

This study presents higher surface energy of the silver paste electrodes, approached by the atmospheric pressure plasma-jet method. This plasma has been produced and exposed in an argon atmosphere with a frequency of 11.5 kHz to check the contact angle after treatment. The visible plasma jet's flow has a length of roughly 16 mm, as shown in Fig. 1. The contact angle analysis was used to determine the hydrophilicity of various silver paste surfaces after plasma treatments[14]. The contact angle was decreased dramatically regarding different treatment times, voltage, and gas flow rates. As a result, the surface energy significantly increased. Data was measured from the contact angle, and the electrode surface became more hydrophilic within a short time after treatment.

Furthermore, for 1 min, we compared the uniform treatment for a large area sample with diverse areas. There was no difference in contact angle for the various regions with plasma treatment. So, this process is quite uniform and assumed to be very useful in forming a stacked structure in manufacturing large-area electronic devices for various applications.

2. Materials and Method

The schematic diagram of the test setup was prepared on an atmospheric pressure plasma jet, and an image of the silver electrodes was fabricated on a glass substrate with a thickness of 1 mm, as shown in Fig. 1(a). The substrate films have the same length and width (2 mm × 8 mm). On the other hand, the silver paste film was around 15.5 μm thick and purchased from Sigma Aldrich, Korea. A relatively small amount of silver paste has been put on the centre surface of glass substrates for electrode preparation with scotch tape attached to the surrounding sides for support. After that, the silver paste was heated for 30 min at 70 ℃ (temperature) on a hot plate, and all "scotch tape" was removed from the glass substrate. Finally, the silver paste surface was ready to be treated with the plasma treatment cleaner.

When the samples were positioned for treatments during the Ar plasma exposure period, the treatments were examined at ambient temperature. Afterwards, it was determined that the sample's temperature reached 40 ℃ after one minute, 50 ℃ for two minutes, and 60 ℃ for 150 seconds, respectively. The temperature was due to the plasma's physical impacts; however, nothing else was physically harmed for up to 150 seconds.

Across the silver electrodes, a high-voltage source of energy (5.5, 6, 6.5 kV) was supplied. Here, the space between the nozzle tip of the plasma jet and the grounded electrode was 16 mm, and the principal working argon gas throughout the operation. The argon gas stream rate was 2, 2.5, and 3 L/min and had an operating frequency of 11.5 kHz. The contact angle of DI water droplets was measured before and after plasma treatment on silver paste electrodes, and the surface energy was calculated using the Fowkes model. In addition, the contact angle was measured using PicPick software after and before atmospheric pressure plasma treatment with various conditions.

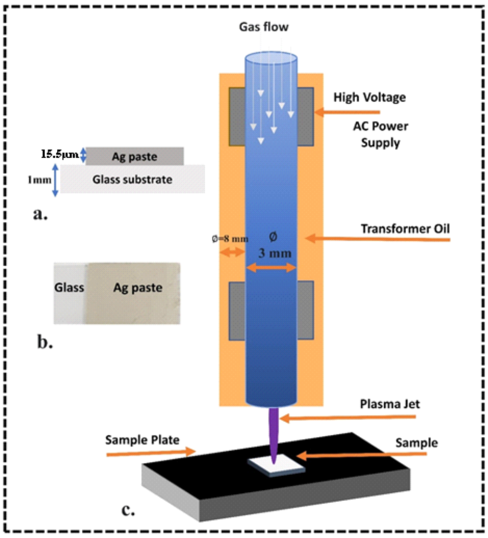

Fig. 1. (a) schematic of cross section view of Ag-paste electrode on the glass substrate (b) Photograph of Ag paste electrode sample, and (c) schematic diagram of the experimental setup of plasma jet.

3. Result and discussion

This experiment looked at the effect of an atmospheric pressure plasma jet on the contact angle of DI water on silver particles and the improved wet ability of a solid surface. Contact angle measurements of plasma-treated and without-treated silver surfaces investigated the wetting response shown in Fig. 2. However, a change in surface wettability was observed after various plasma treatment

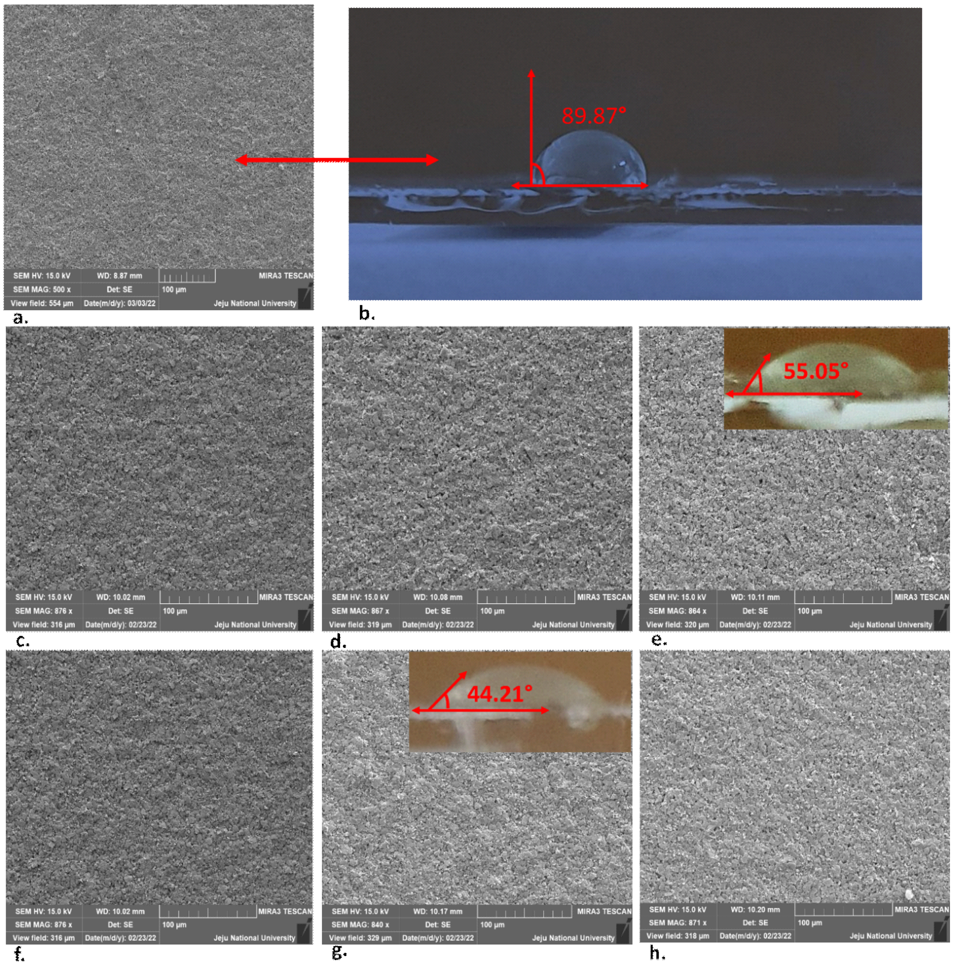

Fig. 2. SEM images of Ag films before and after plasma treatments. a) SEM image without treatment, (b) water drop before treatment, (c–e) with treatment after applying 5.5, 6 and 6.5 kV, and (f–h) with treatment after applying 60, 120 and 150 sec.

conditions. The wettability of atmospheric argon plasma treatments is higher than that of O_2 plasma, allowing for better contact with a surface. Plasma treatment is much more hydrophilic on silver surfaces, as seen in the water contact angle than untreated silver films. When reactive gases such as oxygen, fluorine, or ammonia are introduced, chemical changes occur; for example, new peroxide, hydroperoxide, carboxyl, or hydroxyl groups are generated at the surface, resulting in the immobilization of additional molecules of interest [16]. Crosslinking predominates when plasma is derived from an inert gas, such as helium or argon [17]. The key distinction is that argon plasma is inert, whereas oxygen is not. As O–atoms may be connected to oxygen plasma, there will most likely be more oxygen on the surface[18]. Other O–groups (–Oh, –COOH...) may arise depending on the material and treatment parameters. Long enduring hydrophilization is induced by Ar plasma than by O_2 plasma[19].

The silver films have been quickly absorbed by the water droplets using capillary effects of plasma treatment, allowing the water to make better contact with the silver layer, particularly oxidation/reduction plasma processes when the silver coating is produced, which would process a liquid moving through a confined space without the help or even in resistance to the external factors such as gravity. It shows SEM images of Ag films at 4 kV (no treatment) and various applied voltages and times (with treatment). The morphology and contact angle of the Ag paste electrode are seen in Fig. 2(a-b); there is a significant variance between Fig. 2(a-b) and others because of no treatment. The untreated plasma on the Ag electrode exhibits a contact angle of 89.87 ° . However, the contact angle loop has been reduced following plasma treatment. Further advancing contact angles determined at a particular time and voltage intervals after treatment are also shown in Fig. 2(e,h). The plasma treatment was utilized to see how it affected the wetting response on the Ag surface.

The shape of the Ag paste can also be seen after applying different voltages of 5.5, 6, and 6.5 kV. As a result, there are more disparities, as seen in Fig. 2(c-e). The plasma's treatment time has grown due to the higher processing treatment time, and it has begun to display some irregular points. Various interrupted points as applied times in all individual electrodes are shown in Fig. 2(f-h). Furthermore, the surface shape was modified after plasma treatment with a specific range of applied voltages and periods.

3.1. Theory of the surface energy of electrode

Various experiments were carried out, and the data were expressed as mean and standard deviation. This data was calculated using Fowkes model.

$$\gamma_s = \gamma_{sl} + \gamma_l \cos\theta \cdots\cdots\cdots\cdots\cdots\cdots \tag{1}$$

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s^d \gamma_l^d)^{0.5} \cdots\cdots\cdots\cdots \tag{2}$$

In recent years, several surface energy-based methodologies have been proposed. According to Fowkes model, the present study analyzed data using equations (1-4). The abilities of treated and untreated electrodes in terms of electricity and electrochemistry. The well-known Fowkes model is used to estimate the surface energy estimates from the contact angle information. We conducted our experimental studies here, and the results were presented as mean and standard deviation. Considering contact angles, the Fowkes model effectively enables the measurement of the surface energy interaction[15]. As a result, we proceeded with this model, which only takes one solution to demonstrate the fundamental change in surface energy. The contact angle values for the four experiments were carried out with the various conditions presented in Fig. 3(a-d).

$$\gamma_s = \gamma_s^d = \gamma_l^2 (1+\cos\theta)^2 / (4\gamma_l^d) \cdots\cdots\cdots \tag{3}$$

$$\gamma_s = \gamma_s^d = 0.25\gamma_l (1+\cos\theta)^2 \cdots\cdots\cdots\cdots \tag{4}$$

The conjunction of equations (1) and (2) produces a method for computing the surface free energy of a surface, according to Fowkes model. After that, which is exemplified by equation (3); in this study, DI water's value was defined as 72.6 mN/m, and besides it is facilized as equation (4). The surface energy of each test sample was computed using these equations. In the present study, various application voltages and times were applied to estimate the surface energy from contact angle values of silver electrodes using the Fowkes model. The contact angle between the substrate and the edge of the water phase has been measured, and d is dispersion in the γ_s^d, γ_l^d.

3.2. Contact angle measurement

The findings demonstrate modifications in the wettability and surface energy of manually placed silver paste electrodes treated or untreated by argon plasma. On samples with

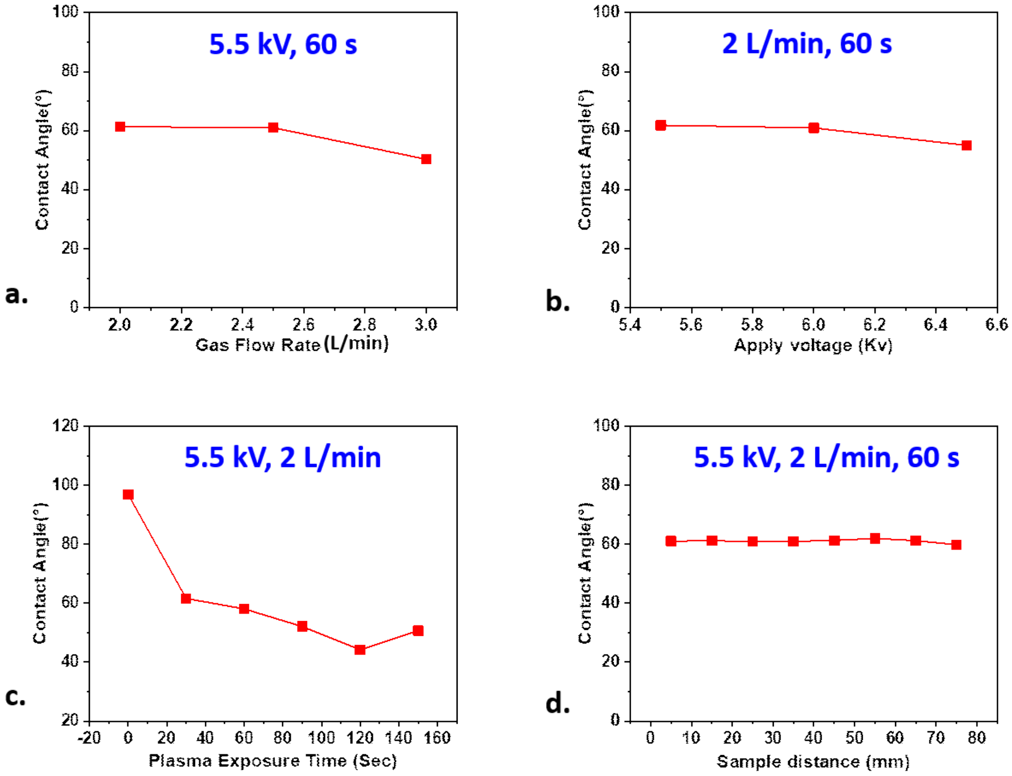

Fig. 3. Contact angle of the on-Ag paste surface (a) with different gas flow rates, (b) with different applied voltage, (c) different plasma exposure time, and (d) uniformity measure for eight different locations of 70 mm sample.

various conditions, we observed the contact angle of liquid droplets and the surface energy of the pieces. Four investigations were performed and substantially influenced Ag surfaces with multiple states. The first study looked at the difference in contact angle as a function of gas flow rate. Under ambient conditions, contact angles were tested on 1-min plasma treated with various gas flow rates. Although gas flow rates were (2, 2.5, and 3 L/min), the contact angle of DI water was determined and found to be 61.35 °, 61.03 °, and 50.33 °, respectively, which differed from the contact angle recorded immediately after plasma treatment. After utilizing 3 L/min gas flow, the contact angle dropped to 50.33 °, as shown in Fig. 3(a). The second is the contact angle difference as a function of the applied voltage with an 1-min treatment. Even though applied voltages were (5.5, 6, and 6.5 kV), the contact angle of DI water was found to be 61.87 °, 60.94 °, and 55.05 °, respectively. Check on utilizing 6.5 kV applying voltage; the contact angle dropped more to 55.05 °, as shown in Fig. 3(b).

The change in contact angle as a function of plasma exposure time was the third factor with various plasma exposure times. While plasma treatment times were (30, 60, 90, 120, and 150 sec), the contact angle of DI water was determined and found to be 61.63 °, 58.08°, 52.1°, 44.21°, and 50.66°, respectively, which differed from the contact angle recorded directly during various plasma treatment time. However, there was more contact angle while the treatment time was 4 kV (without treatment).

The contact angle of DI water was 89.87 for 4 kV, which means no plasma treatment on 4 kV. The contact angle was reduced to 44.21° after treatment with 120 sec, as shown in Fig. 3(c). Fig. 3. shows the test results for the change of contact angle to gas flow rate, variously applied voltages, treatment time, and distance of each sample. When plasma treatment time, voltage, and gas flow rate were increased, the water contact angle of DI water droplets reduced dramatically, showing whether the surface free energy was lower or higher. The initial findings demonstrated that discharge argon plasma treatment might be a valuable method for improving the surface free energy of silver electrodes by modifying their surface properties and boosting adhesion interactions along with polar substrates.

3.3. Surface energy measurement

The contact angle of DI water (liquid) droplet on a material is a promising approach for determining the hydrophilicity of a surface. PicPick software was used to monitor the contact angle of water before and after atmospheric pressure plasma treatment and subsequently examine the Ag electrode surface energy. The contact angle was obtained, 0.01 cc DI water was injected into each sample, and the mathematical formula was used in the findings section. The contact angle was lowered following plasma treatment on silver electrodes, and the surface energy was raised significantly.

Fig. 4(a,b) shows a combination of the contact angle and the surface energy with various applied voltages and treatment times. The surface energy of electrodes was calculated using Fowkes extended model. The results have noted that the contact angle of DI water has lower surface energy. According to the results from the Fowkes model, surface energy (γ_s) of the Ag electrodes are the most minor when applied voltage and treatment time are less, and surface energy has increased after more plasma exposure time or the voltage to the samples. In the meantime, the results from Fowkes model show the surface energy is initially.

However, more studies have been presented to understand the effect of plasma treatment in different situations. The surface energy of

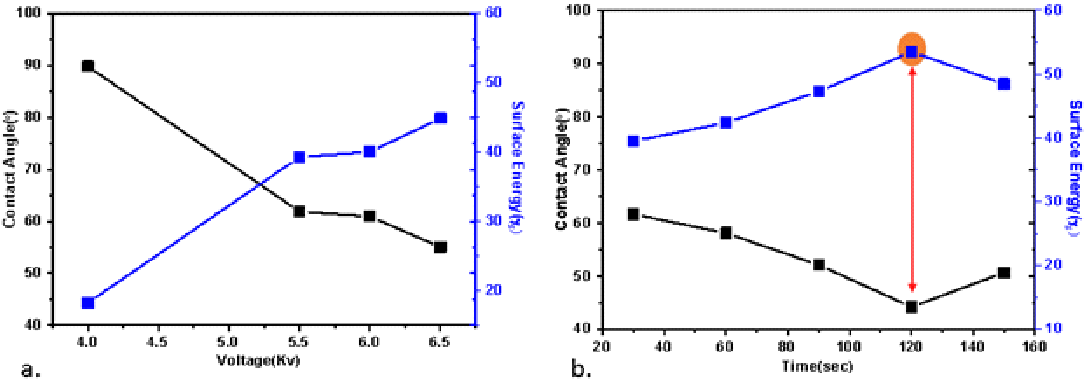

Fig. 4. Contact angle and surface energy with changing (a) applied voltages and b) varying treatment periods.

the Ag solid electrode has been increased to 55.58 mJ/m^2 dramatically when the exposure time was 120 sec; it is shown in Fig. 4(b). However, the more contact angle (89.87 °) clarified when applying voltage was 4 kV, as shown in Fig. 4(a). Moreover, surface energy was increased to 44.901 mJ/m^2 when the applied voltage was 6.5 kV.

In addition, contact angle observations of plasma-treated silver films investigated the surface energy evolution. Compared to varied applied voltages and treatment times, silver surface produces a more hydrophilic; these films have higher surface energy by decreasing the water contact angle. However, as shown in Fig. 4(b), it has increased surface energy until 120 sec following the various plasma treatment intervals.

3.4. Uniformity measurement

The final experiment presented the contact angle of water droplets on the large area of the silver electrode, which has changed a slight variation as a function of sample distance. As shown in Fig. 3(d), the experiment was compared after plasma treatment for eight separate regions taken with the same procedure from different locations to a large area of silver paste electrode. The measuring electrode was up to 70 mm with 2 L/min of argon gas flow rate and an applied voltage of 5.5 kV. However, the treatment time was 1 min for atmospheric pressure plasma to the surface of each Ag paste electrode point. The contact angle of the water drop was assessed to be between 59.86 ° and 62.01 ° . These angles on the treated Ag surface were measured at various points on the surface. The progressing average contact angle was about 60.5 ° with a broad area of 70 mm, smaller than the untreated base plate (89.87 °). This result is consistent with the fact that there were fewer variances between the plasma head and different sections of the Ag surface. The contact angle was reduced, although plasma lead was employed in each sample location. As a result, the contact angle does not alter considerably for a large area sample. This method was performed without the effect of a wide-area example of the silver paste electrode. Consequently, discharge air plasma does not change the contact angle of the large-area sample, and this process has been uniformed for a significant area of the Ag electrode.

4. Conclusions

In summary, we applied an atmospheric pressure plasma jet method to increase hydrophilicity, creating more surface energy for Ag electrodes in different situations (voltage, time, gas flow rate, and large area sample). After plasma treatment, the electrode surface becomes more hydrophilic quickly. Moreover, the film measured uniformity for surface energy with eight locations, for example. We demonstrated more surface energy on silver paste electrodes by the atmospheric pressure plasma jet method. We observed no difference in the contact angle of a large-area sample within a short period. The plasma treatment method is appropriate for potential such as low cost, ability to deposit any surface, the rapid development of electronic technology, etc. The plasma treatment method resulted in higher surface energy with uniformity for large-area samples, which can be used in various electronic applications without damaging the Ag electrode physically. The field of wide-area electronic component manufacturing and related technologies is determined to benefit significantly from the work that has been expressed.

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