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Simple Fabrication Method to Produce Flexible Electrode Capable of Soldering

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We have developed a simple method of producing a customized flexible electrode that is capable of soldering. This method consists of a few fabrication steps. The first step is the laser printing of a reversal pattern of the electrode on a thermally resistant plastic film. The second step is electron beam evaporation to fabricate multilayered metals, such as Ni-Ag, on the film. The third step is a kind of liftoff process, which is the removal of unnecessary metals together with the underlying toner by sonication after immersing the film in an organic solvent. After a thorough washing, we can obtain the desired patterned-electrode film. Several film electrodes were fabricated by this method. Consequently, some electrodes tightly adhered to the basal film and endured soldering by careful choice of the combination of metal layers. Although the conductance of these electrodes was less than the expected value estimated from the bulk metal conductance, the method can be used for the development of small electrodes. This time, we fabricated electrodes with several metals such as Ag, Au, and Pt at the surface, which seem not only useful as sensor electrodes but also as electrode pads. The method also may be useful for developing sensors on the laboratory scale.

1. Introduction

Today, flexible electrode substrates are widely used in various electronic devices. They are often used at the joints of moving parts, such as the hinge of a foldable laptop computer and mobile devices. Flexible substrates are also used as connecting cables inside many electronic devices to simplify the assembly of multiple electronic components in a limited space. For example, they connect the main circuit board and liquid crystal display (LCD) panel in liquid crystal televisions. Moreover, flexible substrates have become important components for wearable devices in order to fit the surface shape of the human body.[1–4]

To develop new wearable devices, we have to prepare customized flexible electrode substrates. Although it is customary to outsource the preparation of substrates, which have most appropriate features and accurate size, it is sometimes more convenient if they are produced in our own laboratory. In the latter case, we have to carry out two types of fabrication. One is the deposition of a conductive material on the substrate, and the other is patterning. We can use several conventional

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methods, such as electroplating, vacuum evaporation, or sputtering, as the former procedure, and photolithography or screen printing as the latter. However, conventional patterning methods often require much time and effort. Recently, inkjet printing using a conductive ink has attracted considerable attention as a new and simple method of preparing electrode substrates.[5] This method enables the deposition of a conductive material and patterning simultaneously. Another simple but uncommon method is the line patterning method (LPM).[6] This method provides electrodes made of organic conductive material on a polyethylene terephthalate (PET) film. The method is a kind of liftoff process using a laser printer as a patterning device. The substantive point is that the toner is soluble in organic solvents such as toluene. The treatment of the organic solvent after the printing and deposition of metal layers removes the metal pattern with the underlying toner. The advantage of this method is that the entire fabrication, including designing the electrode pattern, is possible to carry out in a day. Therefore, it may promote development cycle of sensors.

In the past, using PET films, we extended the LPM to prepare various metal electrodes for homemade sensors such as glucose sensors[7,8] and shear force sensors.[9] This time, we further explored the method to prepare electrode substrates that are capable of being soldered.

2. Materials and Methods

2.1 Fabrication of electrode pattern

Electrode fabrication consisted mainly of three steps (Fig. 1). The first step was the printing of a reversal pattern of electrodes on a substrate film. A laser printer (Seiko Epson Co., LP-S5000) with its standard toner cartridge (black toner) was used for printing. In most experiments, a thermally resistive polyimide film (Du Pont-Toray Co., Ltd., Kapton®, thickness: 50 μm) was used

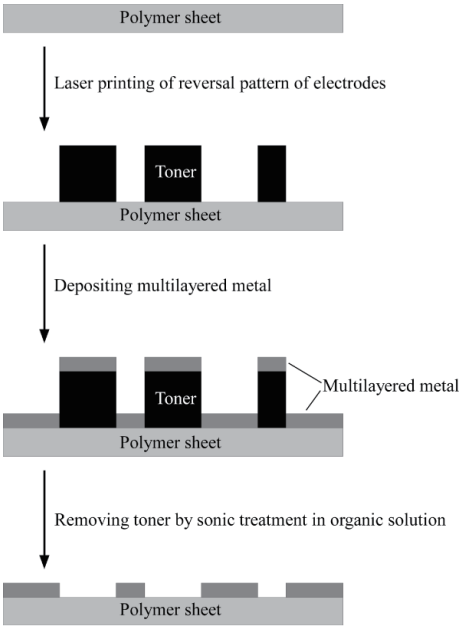


Fig. 1. Fabrication of electrodes on flexible film. There are three main steps. The first step is laser printing of reversal electrode patterns. The next step is electron beam evaporation of multilayered metals. The final step is a lift-off process. Unnecessary metal is removed with underlying toner by dissolving it in organic solvent.

as the substrate for electrodes. In some experiments, we used a PET film for comparison. After printing, metal layers were fabricated using an electron beam evaporator (ULVAC, Inc., EBX-8C). Evaporation was carried out at a pressure below 5×10^{-5} Torr. Multi-layered metals were fabricated by exchanging the source metals without opening the evaporation chamber. The thickness of each metal was controlled automatically using a quartz crystal microbalance (QCM) thickness monitor (ULVAC, Inc., CRTM-5A), which was installed in the evaporator. After evaporation, the film was cut into small pieces and put into a small bottle filled with acetone. Then, the bottle was soaked in an ultrasonic bath and sonicated for several minutes. Finally, the sheet was gently washed with pure water and then gently wiped with an ethanol-containing tissue. We fabricated various samples on which line patterns with different widths and multi-layered metals were deposited.

2.2 Measurement of width of line patterns

The line pattern of the sample was photographed with a scale, and the width was estimated from the photograph using measurement software (freeware of NIH, ImageJ 1.47v).

2.3 Adhesion test method

The method of adhesion test is explained as shown in Fig. 2. The preparation of the test sample is shown in Fig 2(a). A metal wire was jointed to the surface of a strip of flexible film (2×5 cm^2), which was coated with multilayered metals. In some cases, the solder was used as a joint material,

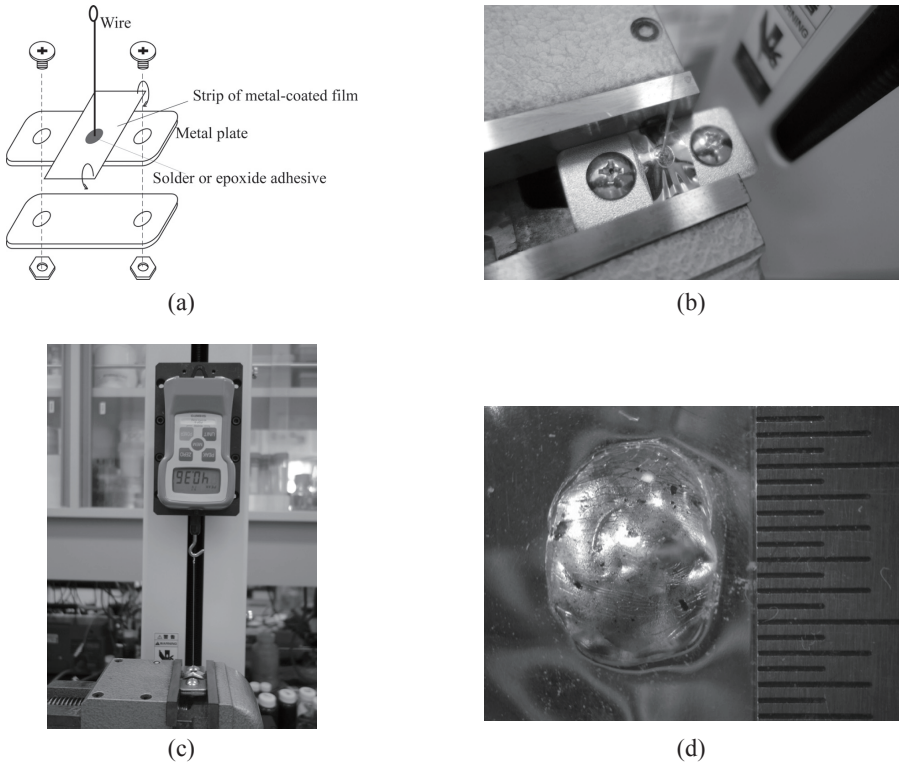


Fig. 2. General view of adhesion test: (a) preparation method of test sample, (b) photo of a test sample, (c) experimental setup for adhesion test, and (d) microscopy image of the attached site with a scale.

and in other cases, epoxide adhesive was used. Then, the opposite side of the film was bonded on a thick metal plate with double-side tape. Both ends of the film were folded back under the metal plate, and another metal plate was placed under the first plate and fixed with bolts. The entire test sample was pinched in a vice [Fig. 2(b)] and placed on a tension tester (Aikoh Engineering Co, Ltd., Model-1308) where a force gage (Nidec-Shimpo Corp., FGP-5) was installed [Fig. 2(c)]. The end of the metal wire was hung on a hook of the force gage. Then, the force gage was vertically pulled up at a constant speed (5 mm/min), and the maximum tensile force (i.e., tensile force at the break point of adhesion) was recorded. After the tensile test, the wire above the adhesion point was cut off, the adhesion part of the wrecked sample was photographed with a scale [Fig. 2(d)], and the adhesion area was estimated from the photograph with measurement software. Finally, the maximum tensile force was divided by the adhesion area to calculate the minimum adhesion strength.

2.4 Measurement of conductance of line patterns

The conductance of line patterns was measured with a digital multimeter (CD771, Sanwa Electric Instrument Co., Ltd. in some cases and 7351E, ADC Co. in other cases). The probes were placed on each line pattern by maintaining a distance of 10 mm, and the measured ohmic value was used to calculate conductance.

2.5 Soldering test

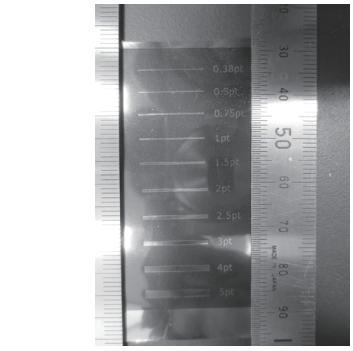
Soldering capability was judged using a commercial solder (H-716, Hozan Tool Industrial Co., Ltd.), which was composed of 60% Sn and 40% Pb. In some experiments, we used flux (HB-20F, Sanhayato Corp.) before soldering.

3. Results

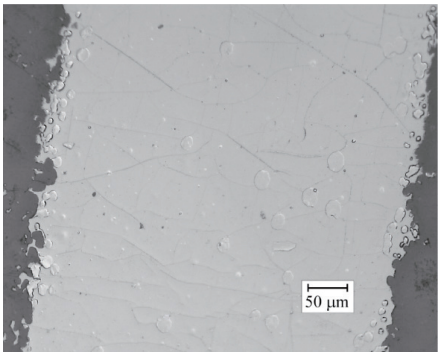
We deposited Cr on a polyimide film in the first trial because Cr is often used as an adhesive layer between Au (or Ag) and other materials. However, the Cr thin film was easily peeled off from the film with an adhesive tape, and we stopped using it in further experiments. Therefore, we came up with a way of using Ni as an adhesive layer instead of Cr. In fact, the Ni thin film could not be peeled off the polyimide film with an adhesive tape.

Figure 3 shows a sample of Ni (thickness: 170 nm) deposited on a polyimide film. At first glance, the patterning resolution seems simply dependent on that of the laser printer. However, the edge of the line patterns seems coarse in the microscopy images [Fig. 3(b)], suggesting that the resolution of the line patterns was dependent on the size of the toner particles. Moreover, we can observe many cracks on the surface of Ni in the microscopy image. Figure 4 shows the measured widths of the line patterns of Ni as a function of their designed widths. Because the edge of the pattern was shaped concavo-convex, we tried to measure the width between the centerlines of both sides. Although the actual width was about 3.5% narrower than the designed width, an almost linear correlation was obtained. To seek the reason for the decrease in width, we checked the size of the film at each step of the fabrication. However, no shrinkage of the film was observed.

The Ni pattern was not peeled off with adhesive tape. However, no line exhibited electric conductivity. Therefore, the Ni layer alone cannot be a candidate electrode. Moreover, it turned out



(a)



(b)

Fig. 3. A sample of fabricated electrode pattern of Ni on polyimide film: (a) entire view and (b) microscopic view of the line pattern with a thickness of 1.5 pt (0.53 mm).

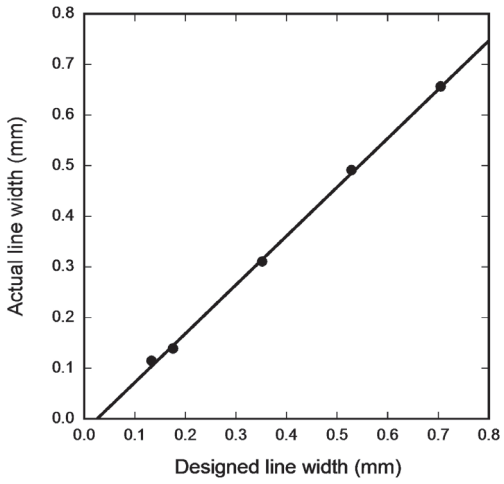


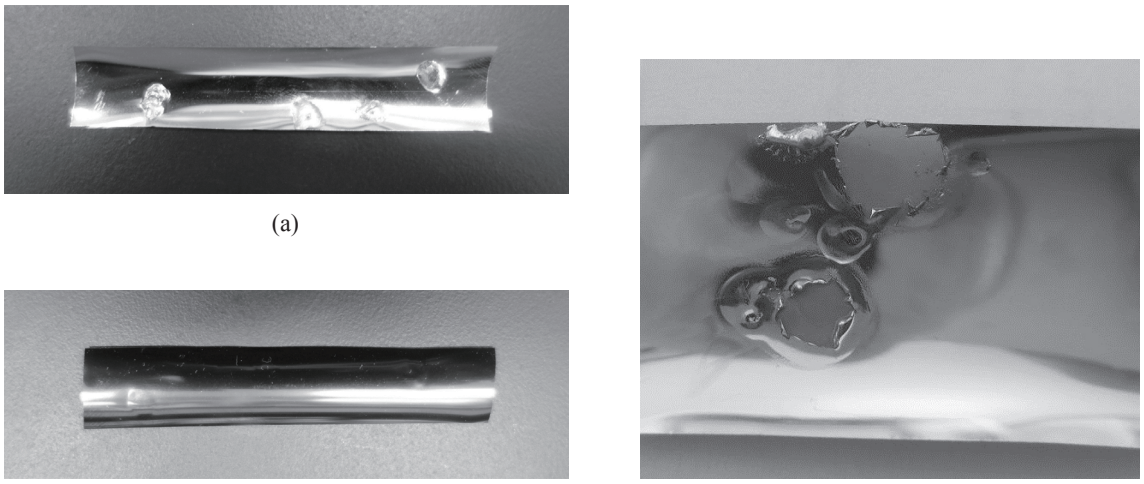
Fig. 4. Correlation between the actual width of the line pattern versus the designed width. The line is obtained by linear curve fitting ($y = -0.0246 + 0.965\,x$, $R = 0.9996$).

that the solder alone was not mounted on the Ni surface, but it was mounted when the Ni surface was pretreated with flux.

When Ag was deposited after Ni on a polyimide film, it was observed that Ni-Ag was not peeled off with adhesive tape, the line patterns were conductive, and soldering was possible. Figures 5(a) and 5(b) show the soldering results of the front and back sides of Ni-Ag deposited on the polyimide film. The photo in Fig. 5(b) clearly shows that the solder did not penetrate the metal layer. Moreover, the pattern was still conductive even after soldering.

When Ni was deposited after Ag, the Ag-Ni could not be peeled off with adhesive tape, and the line patterns were conductive. However, when soldering was carried out on Ag-Ni, the thin metal layer was absorbed into the solder [Fig. 5(c)]. On the basis of these results, we realized that the deposition sequence of metals was important for soldering capability. Thus, we carried out further testing experiments with various combinations of multilayered metal-deposited films.

Multilayered metal patterns such as Ag-Ni (100-200 nm), Ni-Ag (100-100 nm), Ni-Ag-Ni (100-100-100 nm), Ni-Au (100-100 nm), Ag-Pt (100-100 nm), and Pt-Ag-Pt (100-100-100 nm) were fabricated on polyimide films. Figure 6 shows the conductance of multilayered metal-deposited films as a function of the designed width of line patterns. All of them exhibited almost linear correlation.



(a) (b) (c)

Fig. 5. Photographs after soldering: (a) front side of a Ni-Ag-deposited film, (b) back side of the same film, and (c) front side of a Ag-Ni-deposited film.

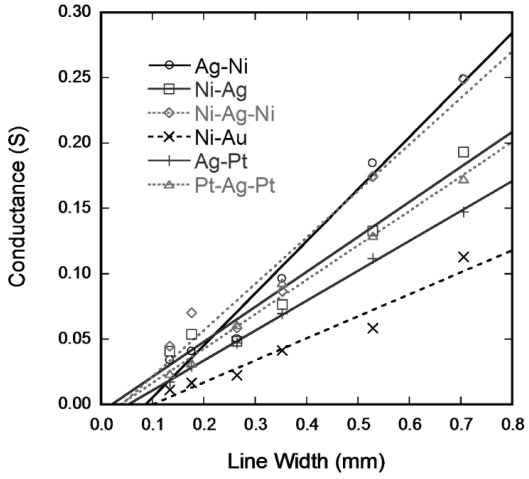


Fig. 6. Conductance of line pattern as a function of width. The lines are obtained by linear curve fitting (Ag-Ni: $y = -0.0346 + 0.399\,x$, $R = 0.989$; Ni-Ag: $y = -0.00571 + 0.268\,x$, $R = 0.978$; Ni-Ag-Ni: $y = -0.0144 + 0.356\,x$, $R = 0.972$; Ni-Au: $y = -0.017 + 0.169\,x$, $R = 0.973$; Ag-Pt: $y = -0.0123 + 0.229\,x$, $R = 0.999$; Pt-Ag-Pt: $y = -0.00984 + 0.263\,x$, $R = 0.996$).

The adherence of the deposited metals on basal films was also evaluated. Because the peeling test of metal thin layers with adhesive tape was merely a qualitative method, a force gage was used for the evaluation of adhesion strength. Table 1 shows the results of the minimum adhesion strength test of multilayered metals on films. Here, the term "minimum" is used because the metals were not peeled off at these values. During the test, events such as the rupture of the basal sheet occurred instead of the peeling off of metals. All of the multilayered metals in Table 1 exhibited particularly

Table 1
Results of adhesion tests of samples with various multilayered metals.

Deposited layers [thickness (nm)]	Sheet	Adhesive agent	Minimum adhesion strength (MPa)	Remark
Ni (170)	Polyimide	Epoxy	0.28	Epoxy pulled off
Ag-Ni (100-200)	Polyimide	Epoxy	0.13	Epoxy pulled off
Ni-Ag (100-100)	Polyimide	Solder	1.26	Further test stopped to avoid damage to gage
Ni-Ag-Ni (100-100-100)	Polyimide	Epoxy	0.34	Wire dropped
Ni-Ag-Ni (100-100-100)	Polyethylene terephthalate	Epoxy	0.33	Sheet ruptured
Ni-Au (100-100)	Polyimide	Solder	0.88	Sheet ruptured
Pt-Ag-Pt (100-100-100)	Polyimide	Solder	1.03	Sheet ruptured

Table 2
Qualitative summary of experimental results.

Deposited layers (nm)	Adhesiveness	Soldering testing	Conductivity**
Ni (170)	○	○*	×
Ag-Ni (100-200)	○	×	○
Ni-Ag (100-100)	○	○	○
Ni-Ag-Ni (100-100-100)	○	○*	○
Ni-Au (100-100)	○	○	○
Ag-Pt (100-100)	○	×	○
Pt-Ag-Pt (100-100-100)	○	○	○

*Adhered only when flux was used.
**Conductivity is indicated as ○ when the measured value at the line width of 0.7 mm was larger than 0.1 S.

strong adhesion (note that the atmospheric pressure is about 0.1 MPa). Ni was a superior adhesive between the polyimide film and Ag/Au in our experiment. Moreover, Pt adhered to the polyimide film and Ag. Because we used PET film instead of polyimide film previously, adhesion tests with a PET film as a comparison sample were carried out. In the case of Ni-Ag-Ni deposited PET film, the multilayered metal tightly adhered to the film.

In addition, a soldering test was carried out and the results are shown in Table 2. In this table, conductivity was judged as acceptable when the value at a line width of 0.7 mm was larger than 0.1S. According to this table, polyimide films deposited with Ni-Ag, Ni-Ag-Ni, Ni-Au, and Pt-Ag-Pt can be used as solderable electrodes.

Because all the experiments explained here were done with lead-containing solder, we carried out further soldering tests using a lead-free solder (H-716, Hozan Tool Industrial Co., Ltd.), which was composed of ca. 99.3% Sn and 0.7% Cu. Polyimide films deposited with Ni-Ag (100-100 nm) and Ni-Au (100-100 nm) were solderable with the lead-free solder.

4. Discussion

Several solderable electrodes were fabricated. The capability of soldering was dependent on the deposition sequence of metals. Soldering was possible for a Ni-Ag-deposited film, whereas it was not possible for a Ag-Ni-deposited film. Although our aim is to simply provide useful electrodes, we would like to hypothesize a mechanism of soldering to explain our results using Fig. 7. In the case of the Ag-deposited film, Ag is easily absorbed into the solder because both form an amalgam. On the other hand, in the case of the Ni-deposited film, Ni does not form an amalgam with the solder, leaving the solder on Ni. However, we cannot use the Ni-deposited film because it has poor conductivity. Moreover, it is well known that the Ni layer alone has a poor solderability surface.[10] In the case of the Ni-Ag-deposited film, it is presumed that the Ag layer forms an amalgam with the solder, but amalgamation does not proceed further with the Ni layer, and the solder remains on the Ni. In the case of the Ag-Ni-deposited film, it is presumed that the solder absorbs the entire thin metal layer.

The relative decrease in the width of line patterns is attributed to the shrinkage of the film due to several reasons. The first is heating during laser printing. The second is heating during the electron-beam (EB) evaporation. And the final one is the treatment with acetone. However, as already explained in the results, we did not observe any shrinkages of the film throughout the electrode fabrication.

We can estimate the theoretical conductivity of each line pattern in Fig. 6 from the specific resistance of bulk metals. For example, the theoretical conductance of Ni-Ag (100-100 nm), with a line width of 0.7 mm and a length of 10 mm, was calculated to be 0.54 S from the bulk specific resistances of Ni (6.84×10^{-8} Ωm) and Ag (1.59×10^{-8} Ωm).[11] The measured conductivity of Ni-Ag (0.19 S) was about a third of the calculated value. Likewise, the calculated conductance of Ni-Au (100-100 nm) from the bulk specific resistances of Ni and Au (2.35×10^{-8} Ωm)[11] was calculated to be 0.40 S. In this case, the measured conductivity of Ni-Au (0.11 S) was also less than a third of the calculated value.

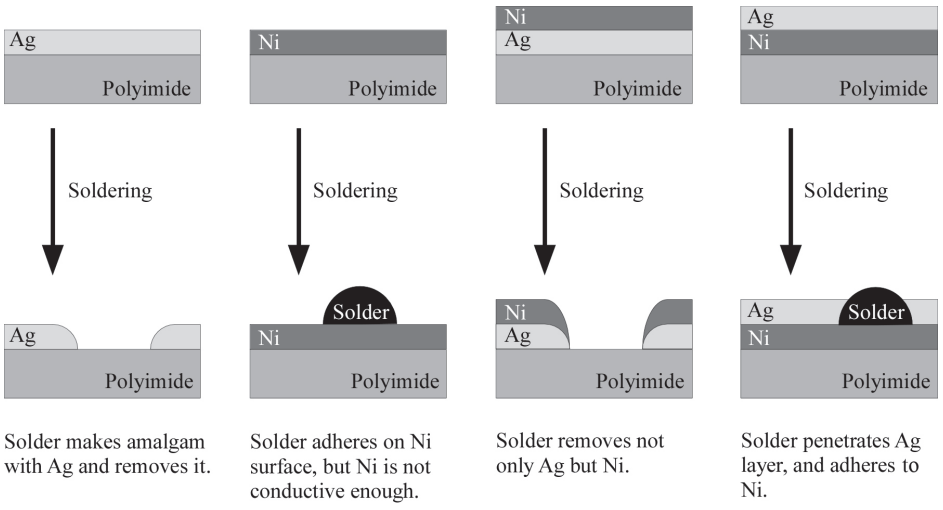


Fig. 7. Tentative hypothesis for the capability of soldering.

In general, the decrease in conductivity of the thin metal layer is mainly attributed to the size effect and structural defects.[10] When the thickness of the metal layer is less than that of the mean free path of electrons in the bulk, the size effect is not negligible. According to the reference, the mean free paths of electrons in Ni, Ag, and Au at room temperature are 420–580, 520–570, and 360–400 Å, respectively.[10] Therefore, the size effect was not dominant in our case because the thicknesses of these metal layers were more than 100 nm in all cases. Therefore, the decrease in conductance could possibly be attributed to a structural defect, such as atomic vacancy, lattice dislocation, and/or generation of grain boundary.

Despite the decrease in conductance, our fabrication method would be useful to develop sensor devices because sensors are usually not large, and thus the loss of conductance of basal metal patterns is negligible in most cases. Particularly in the case of chemical sensors, often noble metals are used as electrodes because they have special features. Our method is suitable for developing chemical sensors because it provides electrodes with a Ag, Au, or Pt surface. In our previous papers,[7,8] we already reported glucose sensors fabricated on a PET film using similar patterning methods with additional processing. In that case, a Pt-based glucose sensitive electrode where glucose oxidase was fixed, a Ag/AgCl reference electrode, and a Pt counter electrode were fabricated. Therefore, it is possible to fabricate such multielectrode-based chemical sensors, which are solderable at the end terminal, if the electrode fabrication method shown here and the post processing written in our previous papers are used in combination.

According to our experience in fabricating sensors,[7–9] it requires only one day to perform the entire process to obtain basal electrode films for sensors including the design of electrodes patterns. The preparation method for electrode films proposed here may enhance the development cycle of sensors in laboratories.

5. Conclusions

We have developed a simple method of preparing metal electrodes on a flexible substrate. This method uses a thermally stable film, i.e., a polyimide film, and presents depositing sequences of metals, thus providing soldering-capable electrode substrates. We can install circuit components and/or connect cables directly on electrode surfaces. Moreover, we can stack multiple flexible electrode films by jointing their edges by soldering. Therefore, this method would be convenient for making prototypes of sensors in the laboratory.

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