Study Report

Selection of suitable material and corresponding processing technique for the production of flexible & stretchable conducting wires, as a part of a electronic circuit embedded in a soft robot.

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Introduction

The world of robotics has so far been dominated by mechanically rigid structure. But as robots have started functioning closer to humans, it is necessary to develop new kind of robots. Soft robots is one such possibility, it refers to robots which are manufactured from soft and compliant materials and do not posses a rigid skeleton. The applications can range from biomedical robots, field research robots, biomemetics to smart prosthetics. There are three main components type in a soft robot namely, robot body, flexible actuators and stretchable electronics. A stretchable electronic circuit is further composed of transistors, conductive wires etc. Hence the realization of a fully stretchable circuit requires stretchable components. But among all of them, conductors are the ones which dominantly effect the stretchability of the overall circuit. In this report I shall present candidate material and processes for the manufacturing of flexible, stretchable conductors for the application in stretchable electronics in the field of soft robotics.

Candidate Materials

As discussed in the introduction, the properties required from the circuit are directly manifested into the component. Although it will be beneficial to obtain stretchable conductors, flexibility is our key issue. The overall performance and stability of the conductor under cyclic loadings will also be the determining factors.

1. Flexible thin films of metals

Wafers of metals do not have the tendency to stretch or bend. But very thin films of brittle materials show flexible characteristics. Although to achieve stretchability special structure have to be fabricated. One of the possible ways of realizing this is by the manufacturing of active device islands connected by specially designed bridges onto the nano scale films or ribbons of silicon. The device islands lets us to fully exploit the electrical performance of metal of high noise immunity and low power consumption. The device islands in themselves are considered rigid but the bridges/interconnections can be of arch or serpentine shape. By decreasing the thickness of the interconnections the stretchability of the matrix can be increased. Stretchability in x and y direction up to 70% has been reported. The limitation arises because of the device islands as the overall elastic behavior and bending limit is inversely proportional to the size of the device islands.

2. Metallic Nanowires

Flexible and stretchable electrodes can be achieved by a matrix of randomly scattered metal nanowires. Among all the materials, Silver is the most preferred one because of its high conductivity. Advantage of metallic nanowires is low cost manufacturing and fabrication and very high conductivity in the range of 5000 to 6000 Scm^{-1} even after successive loadings. The key issue for Silver nanowires is their environmental stability as Ag has high tendency to form oxide or to react with traces of H_2S present in the air. Due to the chemical change the conductivity of silver nanowires decrease drastically. Also nanowires show drastic change in response to mechanical deformation and thus are not suitable for application requiring cyclic loadings and precision working.

3. Conducting Polymer

Organic polymers which can conduct electricity upon chemical doping are referred to as conducting polymers. The advantage of conducting polymers is their property to disperse in a wide range of solvents. Certain polymers have been developed which demonstrate conductivity in the range of 500 – 1000 Scm$^{-1,}$ which rivals that of the transparent conducting oxides. Conducting polymers are fit to a wide range of fabrication techniques such as including inkjet, pre-metered coating applicators, and spray coating thus enabling easy large scale processing and manufacturing. The major disadvantage is that conducting polymers have very bad electrical stability and have the tendency to lose their conductivity in response to UV light or humidity.

4. Graphene conducting films

Graphene is a 2-D allotrope of carbon with planar construction similar to that of graphite. It can act as semi-metal and can achieve substantial optical transparency with high elasticity. Graphene conductor films are stacked sheets of individual Graphene layers which are transferred on organic substrates(such as polyethylene terephthalate) and coated with thin layer of PDMS. Graphene films produced in this manner show properties such as ∼30 /square resistance with 90% optical transparency , with bending radii as small as 2.3mm. Tests done on the best graphene films produced have shown that this material is capable of sustaining its conductivity for up to 11% stretching.

5. Single walled carbon nanotubes(SWNT's) based elastic conductors and flexible films

SWNT's are the tube like structure which result from the curling of 2-d graphene. SWNT's can serve both as conductors and semiconductors in an electrical circuit while showing remarkable bending and stretching behaviors. SWNT are mainly of three type: Armchar, Chiral and Zigzag. Depending on the structure type the tensile strength can range from 94 to 126 GPa. While the Young's modulus for the material is from 92 to 94 TPa. Also SWNT can withstand a pressure up to 24GPa without any deformation. Except for Armchair, which is metallic, all other nanotubes are semiconducting. Thus for our application, armchair type SWNTs will be suitable. To improve the elasticity and durability of SWNT, they are coated with PDMS layer. The resulting substance is referred to as elastic conductor. The elastic conductor can be used as stretchable wires or contacts in electronic integrated circuit. As reported so far, the SWNT based elastic conductors can be stretched by more than 100% and have shown conductivity of 102 Scm^{-1}. Another way to realize SWNT based conductors is by using SWNT thin films. These films are simply dispersion of CNTs onto a membrane during processing which can then be transferred to a substrate by various methods. The advantage of thin films is the easy and cheap manufacturing of uniform and thickness controllable films. Also it means that we do not have to deal with low viscosity issues of gels or inks as in the case of elastic conductors in relation to circuit printing techniques.

Discussion

Table 1: Relative comparison of candidate materials

Material	**Thin Metal Films**	**Metallic Nanowires**	**Conducting Polymer**	**Graphene films**	**SWNT based films & conductors**
Conductivity (S cm-1)	4100~3100	5000~6000	500~1000	___	54~6600
Flexibility	Moderate	High	High	High	High
Stable electric stretchability limit (%)	~100	~30	___	~25	>100 (films)
Stability/strain	Good	Bad	Bad	Bad	Moderate
Printable	No	___	Yes	___	Yes
Cyclic loading performance	Good	Bad	Bad	___	Best

"___" Not enough data available. Data obtained from various sources. Should not be used in standard comparison of material. Values may vary depending upon different processing techniques.

Apart from some limitations mentioned in the previous paragraphs for individual materials. Here I will compare the materials on an overall scale. Both metallic nanowires and conductive polymers show low environmental and conductive stability hence not being suitable for the required application. The silver nanowires[4] showed a drop in conductivity from ~8130 to ~5285 S cm^{-1} after only a few strain cycles in range(0 to 50%). While the elastic conductors[11] did not show conductivity change after 1000 stretching cycles at 70% strain. In elastic conductor[10] the conductance did not change for 30 cycles at 70% change, while at strain > 70% any change in conductivity was attributed to exfoliation of printed Ag electrodes from plastic substrates. The graphene film[6] showed change in resistance due to change in the electronic band structure of grahene just above 25% strain, thus making it possible to induce permanent damage to the graphene film. But even the thin metal mesh[3] showed electrical stability for 1000s of cycle. The CNT films[9] showed an initial 10% rise in resistance but remained constant after repeated stretching cycles in range 5 to 10%. Although it suffered fracture at 25% strain. In the CNT film[8] After an initial conditioning strain cycle, in which conductivity decreased ~6% with increasing strain, the nanotube/elastomer sheet was repeatably deformable over 100% strain without any significant change in conductance. By comparison the overall stability of SWNT based conductors and thin metallic meshes is very high over repeated stretching cycles.

In metal mesh the stretchability is limited only to specific orientations, more complex shapes have to exploited for accommodating more stretching configurations. Even so the low strain and mechanical stability of metals like Si means that the strength capabilities are far less than that of SWNT based conductors. In CNT film[8] A densified stack containing 18 identically oriented sheets had a strength of 465 MPa/(g/cm3). In CNT film[9] A standard mandrel bending test showed that the sheet resistance of a CNT film remained unchanged after being wrapped around a 2 mm diameter mandrel, while the ITO film started to crack at 8 mm. A standard pen hitting durability of two touch panels, one with CNT/PET and ITO/glass electrodes, and the other with ITO/PET and ITO/glass was carried out. The all ITO panel failed after ∼ 60,000 hits, and the CNT panel had no change up to 1,000,000 hits.

Graphene films have shown remarkable performance as semiconductors but its usefulness as a conducting flexible sheet is yet to fully realized because of the limitations in the processing techniques. Whereas certain printing and deposition techniques have already been developed with regard to SWNT which allow the realization of highly elastic transparent conductors and continuous thin films. Although the conductance of elastic conductors is poor with respect to thin metal films the superiority of SWNT based conductors over metal based thin film is evident due to the strain and strength capabilities of SWNT. Tests have shown that elastic conductors/thin films are able to maintain electrical contact even after being crumpled up. The integration of these conductors/films into the emerging field of organic transistors is much more lucrative than the pseudo flexible field of thin metal oxide films.

Candidate processes and selection of process

SWNT based conductors have two major types, elastic and thin flexible films. Both of these types show different characteristics in terms of overall conductivity, flexibility and stretchability. But apart from performance, we also have to keep in mind other factors such as efficiency and cost. As most of these materials are in their research phase, data linked to the other factors is not readily available, hence for now we will focus on the properties of the resulting material as a screening and selection criteria. The processes I discuss are for the manufacturing of elastic conductors/flexible films and do not focus on the synthesis of the SWNT itself. As most of these processes are applicable to a range of SWNT which have been synthesized by different methods.

1. Drawing thin film from vertically grown SWNT forest[8]

In the research I followed. The team uses carbon nanotube forests that were synthesized by catalytic chemical vapor deposition, using acetylene gas as the carbon source. The CNTs were 10 nm in diameter, and the range of investigated forest heights was 70 to 300 mm. Draw of the sheet was initiated using an adhesive strip from the forest sidewall. The team achieved an average draw speed of 5m/min, with maximum at 10m/min. The sheet width is limited by the width of SWNT forest. But the bigger limitation is that we cannot produce continuous sheets SWNT conductor. The sheet resistivity was Ãˆ700 ohms per square in the draw direction.

2. Roll to roll coating method[9]

Ink considerations for roll to roll method

Most CNT inks which are processed using methods like, vacuum filtration, spray coating etc are prepared using a single surfactant or dispersant. An ink suitable for industrial level application contains CNTs, water, surfactant, viscosity controlling modifiers, humectants for the regulation of drying characteristics, defoam or antifoam agents, wetting agents to reduce surface tension and enhance the spreading on the substrate, adhesion promoters, and biocides to inhibit fungal and bacterial growth. Most of these additives are removed after coating is formed in order to maximize the conductivity of the CNT layer.

Roll to roll deposition technique

Roll to roll method is the application of a thin film of functional material onto a substrate. While the substrate is being transferred from one roll to another, the film of SWNT ink is applied onto the substrate and dried. This method allows for industrial level continuous fabrication of thin conducting sheets.

3. Processing of fluorinated SWNT conductor using grinding and mechanical punching[10]

The SWNT bundles are mixed with an ionic liquid and subjected to grinding giving rise to black paste like substance referred to as "bucky gel". The gel is added to 4-methly-2-pentanone and a fluorinated copolymer(vinylidene fluoride-hexafluoropropylene copolymer) and the mixture is stirred sonicated. The resulting swollen gel is poured onto a glass plate by drop casting and then air-dried(removal of solvent) to obtain a composite film. The SWNT film so obtained is flexible and tensile, but it has low elasticity. In order to improve its elasticity, it is mechanically processed with a numerically controlled punching system and transformed into a perforated film with a net shaped structure. Subsequently, it is coated with dimethyl-siloxane–based silicone rubbers [polydimethylsiloxane (PDMS). The resulting composite material is referred to as an "elastic conductor." Its elasticity is determined by the elasticity of PDMS, which is 6 N/mm^2.

4. Processing of elastic SWNT conductor using jet milling[11]

Jet milling is the process of reducing grain size by the application of jet of suitable gas. The advantage of this process over conventional grinding of SWNT is its less intense nature. Thus the processesed SWNT fibers are longer and allow higher conductivity of the elastic conductor. In this method SWNTs of high purity, an ionic liquid and 4-methly-2-pentanone are stirred to produce a swollen gel. The gel is then processed on a high-pressure jet-milling homogenizer, giving the black paste of bucky gel. To the bucky gel is added 4-methly-2-pentanone and a fluorinated copolymer, vinylidenefluoride–tetrafluoroethylene–hexafluoropropylene. The mixture is stirred and poured onto a glass plate by drop-casting and air dried to afford a SWNT–rubber composite gel. The SWNT gel is patterned on rubber sheets made of a silicone elastomer (polydimethylsiloxane, PDMS) using screen printing through shadow masks. The patterned SWNT gel is air dried to afford fine SWNT-based elastic conductors with a linewidth of 100 μm. The printed elastic conductors can be stretched by approximately 100% without any mechanical damage or delamination from the PDMS matrix.

Discussion

The roll to roll method can coat films up to 2m wide at a speed of 500m/min. The drawing technique can accomplish a speed of 10m/min by winding the sheet on a rotating centimeter-diameter plastic cylinder. Although the width of the film becomes less constant at higher speed in draw method. The overall processing time for elastic conductors can take several hours for the grinding and stirring(1-3 hrs), air drying(>12hrs) and patterning but the resulting conductor can be very finely printed. The jet milling process can give gel capable of being printed with a linewidth of 100µm. After ethanol evaporation the thickness of CNT films in drawing method can decreased from ~20µm to 50nm without any considerable lateral changes. While the dry and wet thickness in roll to roll method are in ranges 5-50nm and 5-50µm respectively.

Regarding the elastic conductors only. In both the processes the stretchability is inversely and conductivity is directly proportional to the content of SWNT inside the elastic conductor. In grinding processes the conductivity is traded for elasticity in the initial manufacturing. The end product is made more elastic by the means of mechanical punching of holes into the conductor. The conductor thus formed has conductivity of 57 Scm^{-1}, and a stretchability of 134%. The conductor can be stretched up to 38% axially, without any significant changes to the conductance. The alternative to mechanical punching of the conductor is to maintain finer and longer bundles of SWNT dispersed in the copolymer. This is realized by the use of jet-milling process. The SWNT content can be increased to 16 wt%, bringing the overall conductance of the elastic conductor to 102 Scm^{-1}, while still achieving a stretching limit of more than 100%. Apart from the performance superiority, the other benefit is that the SWNT composite gel is increasingly viscous (more than 10 Pa s), and consequently this material can be finely patterned using direct printing technologies.

Even after the high stretchability in the end product of elastic conductor processes. The overall conductivity(maximum reported is 102S/cm) is minuscule as compared to 6600S/cm(and even higher have been reported in films). Although the CNT films in roll to roll method fail at 25% strain. The drawn films show tensile strengths of 465Mpa. Also as discussed in discussion for candidate materials the elastic conductors from jet milling did not show conductivity change after 1000 stretching cycles at 70% strain. In elastic conductor from grinding the conductance did not change for 30 cycles at 70% change. The CNT films from roll to roll method showed an initial 10% rise in resistance but remained constant after repeated stretching cycles in range 5 to 10%. Although it suffered fracture at 25% strain. In the drawn CNT films, after an initial conditioning strain cycle, in which conductivity decreased ~6% with increasing strain. The film showed no significant change for strain up to 100%. Making the elastic conductors far more stable in case of repeated loading.

Even after the higher stability of elastic conductors the overall conductance is so low that it is clear benefit to work with CNT films as of yet. The high conductivities and fast processing methods of films mean that it is far more affordable to work within the decreased stable electric range, which is still larger in magnitudes than the highest possible conductivity of elastic conductor. Also the roll to roll method is not only far more controllable with respect to film width than drawing, the range of thickness is also far less. The drawn film showed a resistance of 700 ohm/square while roll to roll method can manufacture sheets with resistance as low as 60 ohm/square.

Conclusion

Among the candidate materials. SWNT based conductors and metal conductors show the highest stability with respect repeated cyclic loading. Also metallic nanowires and conductive polymer show low environmental stability as they are highly reactive and require specialized coatings. The overall stretching capabilities of SWNT based conductors lies in ranges of 25% to > 100% which is far superior than most other materials. Also SWNT films have shown strengths up to 465Mpa, which is far from realization in thin metal meshes. The overall advantage in flexibility, stability, conductivity and strength makes SWNT based conductors the most suitable for the desired application

In processing of the SWNT based conductors, I had to chose between two types of conductors. Namely thin films and elastic conductors which are a direct realization of the processing techniques. Although the elastic conductors offer a wider stable electronic range, the incredibly fast processing techniques related to thin films(up to 500m/min) and the much higher conductivity range of thin films means that it is far more beneficial to follow SWNT thin films rather than elastic conductors. Among the processes for thin films, roll to roll coating is not only the fastest but also more controlled in regards to the width and thickness of the film. One roll to roll coating plant running at full capacity can possibly provide for half the current touch panel market. The disadvantage of roll to roll method over draw method is the overall strain capability with 25% and 100% respectively. Also films produced by draw method show 6% change in resistance, this value goes up to 10% in case of rolled films. Still considering that the drawn films show resistance of 700 ohm/sq while rolled film show 60 ohm/sq, the numerical change in resistance of rolled films is much smaller. Thus relatively roll to roll method is currently the most efficient process for producing SWNT based thin films.

SWNT is currently one of the most promising materials for the future which reserves the capability of being semiconductor and conductor. It can prove to be useful for a wide range of applications, which can be achieved by simple variation in the processing technique of one type of SWNT to another type. The adaptability and the availability of fast processing methods means that SWNT based circuits can easily and efficiently share the market load of current Silicon based circuits. It is obvious that although SWNTs are not going to completely replace metal and Silicon based circuit but the ongoing and further research will open new potential areas of application. The field of organic circuits is lucrative for its application not only in robotics but also in various other fields like flexible displays, eye cameras, stretchable bioelectronics, and epidermal electronics to name a few.

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