Gold Coating of a Plastic Optical Fiber Based on PMMA

Seok Min Kim, Sung Hun Kim, Eun Ju Park, Dong Lyun Cho, and Moo Sung Lee

Faculty of Applied Chemical Engineering and Center for Functional Nano Fine Chemicals,
Chonnam National University, Gwangju 500-757, Sourth Korea
`smk0706@hotmail.com, chollado@naver.com, jjpeunju@chonnam.ac.kr,`
`dlcho@chonnam.co.kr, moosung@chonnam.ac.kr`

Abstract. We investigated the adhesion between gold thin film and poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-co-HFP)) substrates with the aim of imparting electrical conductivity to plastic optical fibers (POFs). The two polymers were used as the core and the cladding of POF, respectively. Gold thin film of 50nm thickness was deposited by ion sputtering onto the polymers and also POF. Several approaches, which were well known to be effective in enhancing adhesive strength between gold and polymers, were applied in this study: introduction of polar functionality on the substrate surface by plasma treatment, buffer layer insertion, and physical surface roughening. The variation of wettability and adhesion with plasma conditions was investigated through water contact angle measurement and cross hatch cut test. Even though the contact angles of substrates were decreased after Ar or O_2 plasma treatment, irrespective of the polymer type, the adhesion of polymers with gold layer was very poor. The Ti buffer layer of 5nm thickness, which was deposited between PMMA substrate and gold layer, did not contribute to improve the adhesion. However, P(VDF-co-HFP) substrates with rough surface of 13.44nm RMS shows 3B class adhesion to gold from the cross hatch tape test. The gold-coated POF showed the electrical conductivity of $1.35\times10^{3}\text{Scm}^{-1}$ without significant optical loss. The result may be used for developing a medical device capable of simultaneously applying electrical and optical stimulus.

Keywords: plastic optical fiber, POF, sidelight, overcoating.

1 Introduction

Light therapy consists of exposure to daylight or to specific wavelengths of light using lasers, LEDs, dichroic lamps or very bright, full-spectrum light, for a prescribed amount of time and, in some cases, at a specific time of day. Laser light waves penetrate the skin with no heating effect, no damage to skin and no side effects. Laser light directs biostimulative light energy to the body's cells which convert into chemical energy to promote natural healing and pain relief. It has proven effective in treating *Acne vulgaris,* seasonal affective disorder, neonatal jaundice, and is part of the standard treatment regimen for delayed sleep phase syndrome [1].

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Acupuncture is a technique of inserting and manipulating fine filiform needles into specific points on the body to relieve pain or for therapeutic purposes. Even though most acupuncture needles are made from stainless steel but can also be made of silver or gold. Among several types, plastic needles made from plastic optical fibers are very interesting because they collect light from the light source and radiate light or heat against the affected body part, producing improved remedial effects [2]. More recently, an optical/electrical acupuncture needle has been introduced for the purpose of simultaneously applying pulsed electrical energy and colored light one into body tissue [3]. The needle body is formed of a central optical transmission core, preferably an intermediate opaque non-conductive clad layer atop the core and an outer conductive layer positioned atop the clad layer.

Plastic or polymer optical fibers (POFs) are fiber type optical waveguides and can transmit light up to several hundred meters. The light transmitted through OF includes digital light pulse carrying digital information, sunlight, therapeutic laser light, and so on. Since optical signal is propagated along the fiber by total internal reflection, POF has core-sheath (or cladding) structure and refractive index of cladding should be lower than that of core, i.e., $n_{\text{cladding}} < n_{\text{core}}$. Usually, poly(methyl methacrylate) (PMMA, $n = 1.49$) and fluoropolymers with $n \sim 1.35$ to 1.43 are used as core and cladding polymers, respectively [4, 5]. Since POF is flexible and tough, it can be used as effective medical devices. For example, flexible light diffusers made from POF can be adjusted during treatment, especially on complex body surfaces unlike many current inflexible light diffusers [6].

In this study, as a preliminary work on the realization of such optical/electrical acupuncture needle, we attempt to impart electrical conductivity to POF by coating gold thin layer on its surface. Gold was selected due to its high conductivity of $4.52\times10^3 \text{Scm}^{-1}$ and aesthetic point of view. Since the cohesive energy of metals is typically two orders of magnitude higher than that of polymers, the interaction between the two is very weak. The durability and performance of the needle is closely related to the adhesion between POF and gold layer. As a prerequisite for the development of gold-coated POF needle strong adhesion between gold and POF is needed. Several approaches, which are well known to be effective in enhancing adhesive strength between gold and polymers, are applied in this study: buffer layer insertion, plasma treatment and physical surface roughening.

2 Experimental

2.1 Materials

Two different polymers, poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-co-HFP)) were purchased from Aldrich Chemical Co. and vacuum dried at 50°C for 24h before use. The two were the same type of polymers, which were used as the core and the cladding of POF, respectively. The POF used in this study was a step index type with the diameter of 0.5mm and obtained from Nuvitech Co., Ltd, Korea.

2.2 Sample Preparation

The polymer substrates having a dimension of 20×20×1 mm were prepared by compression molding using a Carver press. In order to reduce the surface roughness of substrates applied during preparation they were annealed at the temperature above the melting and glass transition temperatures of the polymers for 20min: at 170°C for PMMA and 120°C for P(VDF-co-HFP), respectively. The surface of the substrates was then modified by using a plasma treatment in a home-made plasma reactor. Three different working gases, Ar, O_2, and a mixture of Ar/O_2 (1:2 by volume) were used in this study. Except for processing time, other processing parameters were kept constant at 60W of plasma power and 30sccm of gas flow rate.

Gold thin film of 50nm thickness was deposited by using a DC/RF magnetron sputtering system onto the substrates, which were plasma-treated or not, and also POF. The system was equipped with two different targets, titanium and gold, and sputtering was performed at the condition of a DC power of 300W and working pressure of 10×10^{-3} mTorr for 30second. The thickness of gold thin layer was controlled to be 50nm.

2.3 Characterization

The effects of plasma treatment conditions (operating gas and operating time) on the surface of the polymer substrates were investigated by using contact angle measurement and X-ray photoelectron spectroscopy (XPS), which is widely accepted as one of the most powerful techniques for polymer surface chemical analysis.

The adhesion of gold layer with the polymer substrates was determined by a cross hatch cut tape test (ASTM D3359-02). The test method was originally designed to assess the adhesion of coating film up to 125μm to substrates by applying and removing pressure. A cross-hatch cutter with multiple preset blades was used to make sure that the incisions were properly spaced and parallel. After the tape has been applied and pulled off, the cut area was then inspected and rated according to the percentage of the squared remaining on the test specimen. In this study, 1mm (11 teeth) cutter and 12.3125N/25mm adhesive tapes were used.

The electrical conductivity of gold-coated POF was measured by using the 4-probe method, where a silver paste was used for the electrical contact.

3 Results and Discussion

Figure 1 shows the change in the atomic force microscopy (AFM) topography of P(VDF-co-HFP) substrates before and melt annealing. The polymer is used as cladding material for POF. The root-mean-square (RMS) surface roughness of the substrate decreases from 13.44 nm to 2.96nm after melt annealing as a result of mass transfer dominated by surface diffusion. Unless otherwise mentioned, the samples with smoothened surface are used for further study.

XPS spectra of plasma treated polymer substrates are shown in Figure 2. For the case of PMMA substrate of Figure 2(a), new peaks are not shown, but relative intensity of the O1s peak to the C1s peak increases after plasma treatment as compared with that of untreated surface. On the other hand, for P(VDF-co-HFP) substrate, a new peak corresponding to O12 atom is clearly seen at the binding energy of 528eV. The contents of O1s atom increase to 6.78% and 5.25% in Ar and O_2 atmospheres, respectively. This indicates the introduction of oxygen atoms onto the hydrophobic surface of P(VDF-co-HFP) and from the result the change in its surface properties is expected. The effect of the type of working gases on the surface functionality of the substrates is not large.

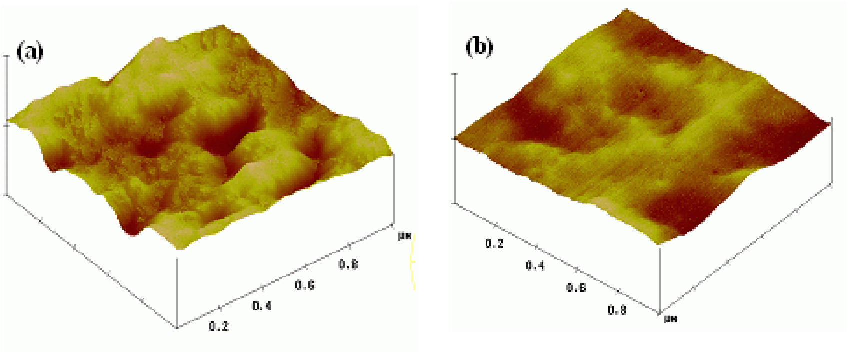

Fig. 1. AFM images of P(VDF-co-HFP) substrates: (a) as-prepared; (b) annealed at 120°C for 20min

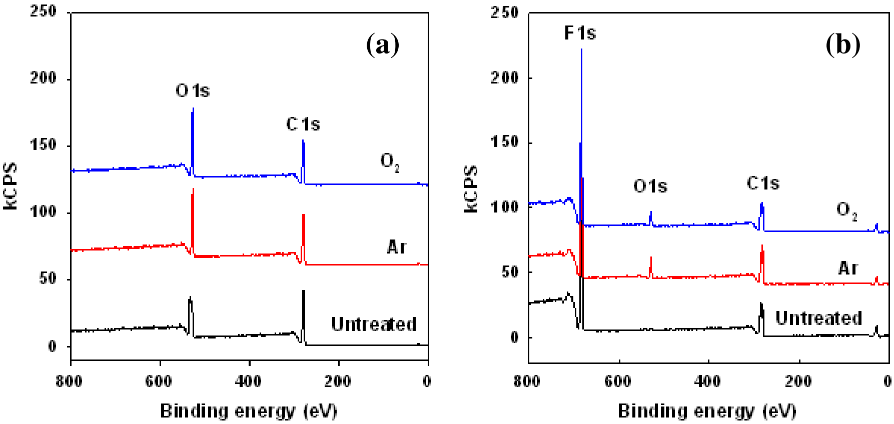

Fig. 2. XPS spectra of (a) PMMA and (b) P(VDF-co-HFP) substrates, plasma- treated at 60W plasma power and 30scm gas flow rate. For visual convenience, the curves are shifted vertically from bottom to top.

Figure 3 shows the variation of water contact angle (*θ*) with the time of plasma-treatment. The measurement was performed after 24h from the plasma treatment, considering that gold thin layers are coated on polymer substrates after the same interval. Irrespective of the type of substrates the angle is decreased at first and then is not changed after 3min treatment. The decrease in the contact angle, i.e., the improvement of the wettability of the polymer surfaces is the result of the increase of the surface polar groups introduced during plasma treatment. The Ar plasma shows a better effect for improving the wettability than the O_2 plasma for P(VDF-co-HPF) substrate, while for PMMA substrate the difference is marginal. This corresponds well to the content of O1s atom introduced by plasma treatment, as shown in Figure 2.

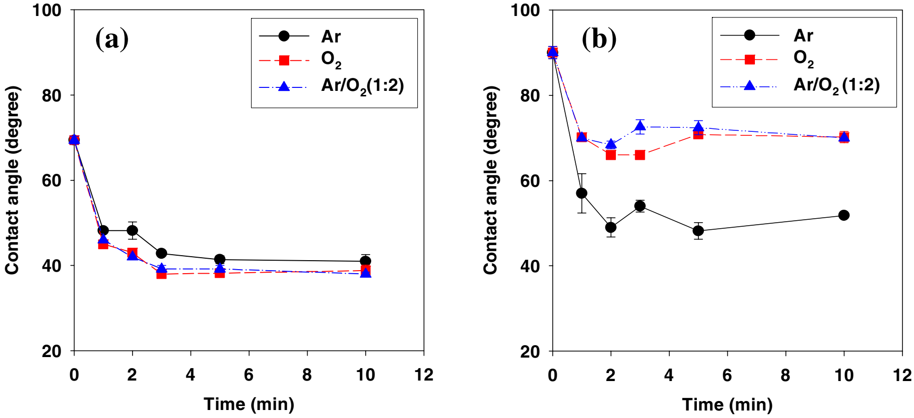

Fig. 3. Variation of water contact angle with the time of plasma-treatment using the working gas of A, O2, or mixture of Ar and/O2: (a) PMMA; (b) P(VDF-co-HFP) substrates

The adhesion between gold and polymer substrates was assessed by the cross-hatched tape test. The surfaces of substrates were treated using Ar plasma for 5min before depositing gold layer. The conditions were chosen because the contact angles did not decrease anymore after the time. Figure 4 shows the photographs of the substrates after the cross hatch cut tape tests. The adhesions of gold thin film to PMMA and P(VDF-co-HFP) were very poor and were evaluated as both classification 0B from the surfaces of cross-cut area from which flaking has occurred. Plasma-treatment condition applied in this study did not contribute at all to enhancing the adhesion. Since the adhesive properties of substrates are affected by their chemical nature, the topography and the cohesive strength of the surface regions [7], no improvement in the adhesion indicates that the functionality introduced onto the polymer surfaces is not enough to change the cohesive energy of polymer surfaces. Extra experiments to introduce different types of functional groups such as thiol group are in progress and the details will be given at the conference.

Figure 5 shows the effect of surface roughness of P(VDF-co-HFP) substrates on the adhesion of gold layer. The substrate which is not melt annealed and has RMS surface roughness of 13.44nm, as shown in Figure 1(a), was used for the test. The change in surface roughness gives significant increase in adhesion: the adhesion level increases from classification 0B to 3B. Since the same plasma treatment conditions are applied, the increase seems to be closely related to the increase in surface area. Although Ar or a mixture of Ar/O_2 gases is well known to be effective etching gas for polymer, the conditions, especially equipment power of 60W, applied in this study are not enough to induce the change in surface roughness. High power equipment and longer processing time are required for the purpose.

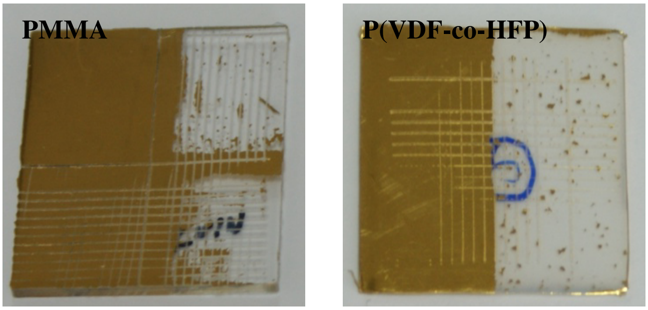

Fig. 4. Photographs of gold-coated polymer substrates after the adhesion test. The substrates with smoothened surface by melt annealing are used for coating.

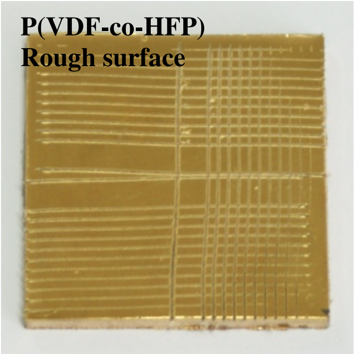

Fig. 5. Photographs of gold-coated P(VDF-co-HFP) substrate after the adhesion test. The substrate with rough surface is used for coating.

POF having the smooth cladding surface of a fluoropolymer, similar to P(VDF-co-HFP) was gold-coated under the same sputtering conditions applied to polymer substrates (see Figures 6(a) and (b)). Plasma-treatment condition applied before sputtering did not change, too. As expected from Figure 4, the gold layer deposited was easily peeled off with bare hand, indicating no adhesion between POF and gold layer. This makes it impossible to use the gold-coated POF as an acupuncture needle capable of simultaneously delivering electrical and light stimuli to the body tissue. Since surface roughness is key factor for improving the adhesion between gold and P(VDF-co-HFP), the surface of POF was slightly damaged by rubbing with sandpaper. The depth and width of the defects introduced was not qualitatively monitored, but the defects is well seen in Figure 6(c). The sample obtained by gold-coating of the specimen of Figure 6(c) is shown in Figure 6(d). It shows strong adhesion not to be peeled off with bare hand. More precise control of surface roughness with controlled manner is required for proper adhesion.

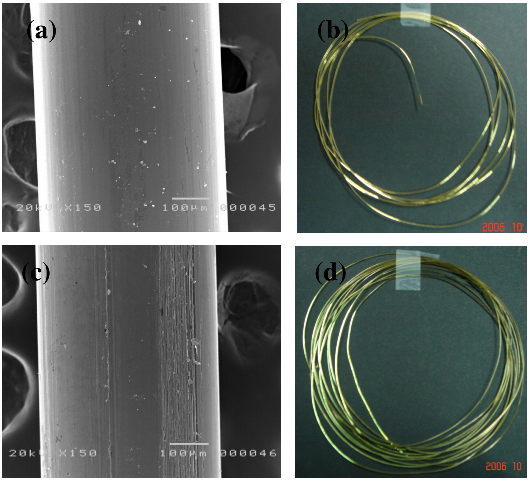

Fig. 6. (a) and (c) SEM micrographs of POF surfaces, (a) neat; (c) slightly damaged with sandpaper; (b) and (d) photographs of the sample obtained by gold-coating of the specimens of Figures 6(a) and (c), respectively

The electrical conductivity of gold-coated POF, which is shown in Figure 6(d), was measured to be $1.35\times10^{3}Scm^{-1}$, one-third of that of neat gold. The optical loss of gold-coated POF did not significantly decrease after physical damaging and gold coating, maybe due to highly reflecting capability of gold.

4 Summary

In this study, we have realized an acupuncture needle capable of delivering optical/electrical stimuli into body tissue. Plastic optical fiber based on PMMA was used as light carrying medium. In order to impart electrical conductivity to POF, gold thin film of 50nm thickness was deposited by ion sputtering onto the surface of POF. From some preliminary works on the adhesion between gold and polymers, it was revealed that surface roughness of polymer substrates is key factor for strong adhesion. Plasma treatment conditions applied in this study was not appropriate and higher power condition was required. The gold-coated POF, in here the surface of POF was slightly rubbed with sandpaper, showed the electrical conductivity of $1.35\times10^{3}Scm^{-1}$ without significant optical loss. The result may be used for developing a medical device capable of simultaneously applying electrical and optical stimulus into body tissue.

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