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# 1. Introduction

## 1.1 Background

### 1.1.1 Alternatives to ITO

Indium Tin Oxide (ITO) have been generally used as a transparent electrode due to its high conductance, transparency, and productivity. However, as the ITO on Earth is running out [1] and has brittle character which restrict flexibility of a device [2], alternatives to the ITO are required. The variety materials to replace the ITO have been developed such as deposition of diverse metal oxide [3-5], conducting polymer [6-7], carbon nano tube (CNT), and graphene [8-10]. Metal oxide such as tin, zinc, titanium, and cesium oxides has been deposited on the substrate using chemical vapor deposition (CVD), reactive evaporation etc. These materials are good for achieving good thermal stability. The vacuum condition, however, has been pointed as an obstacle for high cost of the process. [11] Although the conducting polymer have been studied due to easy and cost-efficient process, it has limit to increase electrical resistivity in harsh condition such as high temperature, humidity etc. Also, CNT or graphene has attracted researchers due to outstanding optical and electrical quality but complex and high-cost

process have been pointed out as their disadvantages. [1] Therefore, it is necessary to develop a material containing stability, easy processibility, and optical and electrical property comparable to those of the ITO.

### 1.1.2 Carbonization from PAN

Carbon materials have gathered much attention from researchers due to its good electrical and chemical properties. [1] Carbon materials through carbonization have been reported abundantly due to advantages of easy and cost-efficient process. The carbonization could be conducted from various precursors. [12-17] Among precursors, polyacrylonitrile (PAN) was studied widely to prepare carbon materials such as carbon nano-fiber and carbon film, since poly-imine ladder polymer which can be carbonized could be achieved through pre-heat treatment at relatively low temperature. [18-19] Therefore, in the study, PAN was selected as a precursor for the carbonization.

### 1.1.3 Imprinting lithography

Conventional photolithography has problems about high cost and difficulty of achieving small nano pattern below 10nm due to light diffraction. Nano imprint lithography (NIL) have fascinated research community as cost efficiency and easy processibility. [20-21] Through the technique, a study about improving the performance such as optical

property due to pattern transfer on objective substrate have been researched. [22] Mainly, thermal imprinting have carried out in the method to achieve pattern at appropriate pressure and temperature above glass transition temperature ( $T_g$ ) using flow of thermoplastic polymer resin. [20-21] Soft mold used as a reusable stamp in the process was made by preparing the replica of UV-curable polymer from nano-patterned hard mold. Particularly, AAO master mold used is made by 2-step anodization, which is achieved by self-assembly of porous alumina at certain temperature and electrolyte applied at specific voltage. Well-ordered pattern in large surface area can be acquired very efficiently and economically. [23]

## 1.2 Purpose of this study

In the study, the carbon film from spin-cast PAN film was achieved by two step carbonization containing pre-heat treatment and carbonization. Conducting film was attained by this easy and cost efficient process. According to PAN concentration, wide range of thickness of carbon film was acquired.

Patterning was introduced to the process to increase its performance, especially improvement of the transmittance. The patterning was conducted by the nano-imprinting. Via nano-imprinting, well-ordered nanostructures in large surface area was obtained cost-efficiently, contrary to conventional lithography such as photolithography. The well-ordered AAO through 2-step anodization was used as the master mold. Replica from the master mold of UV-curable polymer was employed as the stamp in the NIL. Subsequently, the two-step carbonization of the patterned PAN film was carried out. As a result, patterned carbon film was attained. This ultrathin carbon film and porous patterned carbon film were expected to apply transparent electrode replacing ITO with more improvement of the performance.

## 2. Experimental

### 2.1 Flat carbon film

#### 2.1.1 Preparation of PAN film

Polyacrylonitrile (PAN,  $M_w = 150,000$  g/mol) and N,N-Dimethyl formamide (DMF, 99.8%, Sigma-Aldrich) were purchased from Sigma-Aldrich. DMF was used without further purification. PAN solution was prepared as dissolving PAN in DMF at 95°C. PAN film was made by spin-coating (3000rpm, 1min) on the 1.5cm × 1.5cm substrate of quartz plate or Si wafer with concentration ranging from 1 to 7wt.% of PAN solution.

[24]

#### 2.1.2 Carbonization of PAN film

The carbon film was achieved by the carbonization of the PAN film through stabilization and subsequent carbonization at high temperature. The Stabilization of PAN films was accomplished at 250°C for 10h in air or under vacuum. The stabilized PAN film was carbonized at 700°C for 1h under N<sub>2</sub> atmosphere. The carbonization was performed with heating rate at 2°C/min from room temperature to 250°C and then successively at 3°C/min from 250°C to 700°C. Then, natural cooling of the obtained the carbon film was conducted. The carbonization condition was

summarized in Table 1. [24]

<b>1. stabilization ( in vacuum )</b>
Stabilization ( 250 °C, 10h )
<b>2. carbonization ( in nitrogen )</b>
Step 1 Heating (RT~250°C , heating rate 2°C/min) Step 2 Heating (250~700°C, heating rate 3°C/min) Step 3 Heating (at 700°C, 1hr)

Table 1. condition of carbonization

## 2.2 Patterned carbon film

### 2.2.1 Fabrication of AAO master mold

Aluminum sheet (Goodfellow, 99.999%) was polished chemically and mechanically to minimize its roughness, since the roughness is an important factor to fabricate nano structure. The Anodized aluminum oxide (AAO) using as the master mold was prepared by two-step anodization. The anodization of polished aluminum was conducted in a 0.3M oxalic acid electrolyte at 15°C and 40V for 12h. A porous alumina film was selectively removed in an etching solution containing chromic acid. Subsequently, 2<sup>nd</sup> anodization was conducted under the same condition as 1<sup>st</sup> anodization. The time of 2<sup>nd</sup> anodization can be controlled to acquire depth of the pore according to needs. The pore of the alumina was widen as dipping the porous alumina in 0.1M phosphoric acid solution at 30°C. [23] (Figure 1)

### 2.2.2 Fabrication of soft mold

Chemically pre-treatment of the AAO master mold should be required, since adhesion between the master mold and the soft mold should be decreased for easy detachment and release of the soft mold from the master mold. Hydroxide groups on the AAO master mold were formed

by irradiating plasma (O<sub>2</sub> 10sccm, forward power 30W, DC bias-300V) using reactive ion etcher (RIE-3000, South Bay Technology,inc.). The irradiated master mold was dipped in 0.5wt 3-Aminopropyltriethoxysilane (APTES) solution for 10min and then cleaned by methanol and dried. Subsequently, PDMS solution (poly(dimethylsiloxane), monoglycidyl ether terminated) was dropped on the sample at 80°C for 4h. That is because reaction between amino ends groups and epoxide group makes the master mold coated as being exposed PDMS ends on the surface. The sample was cleaned by isopropyl alcohol and dried. UV-curable polyurethane (PU)-based polymer (MINS 311-RM, Minuta) was poured on the chemically modified master mold using a transparent PET film as a support layer of the soft mold. Irradiation of UV light in the average wavelength of 365nm was carried out on the sample to cure the pre-polymer and then a soft mold with PET film was detached from the AAO master mold. [22] (Figure 2)

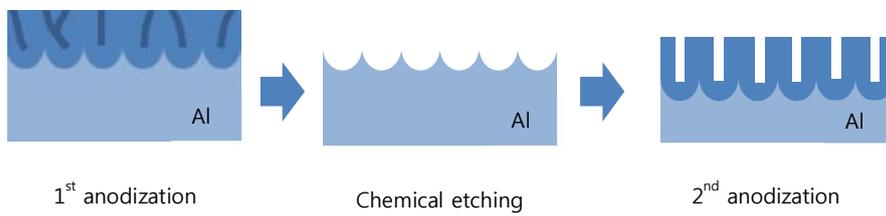


Figure 1. Schematic diagram of preparing master mold through two-step anodization

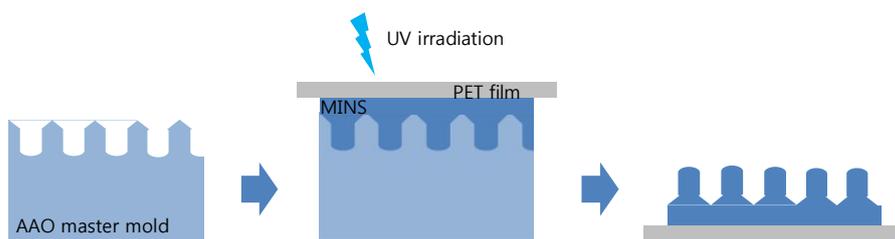


Figure 2. Schematic diagram of preparing soft mold from master mold

### 2.2.3 Imprinting

The soft mold was modified chemically as mention above. The PAN film was prepared by spin-coating (3000rpm, 1min) on the 1.5cm × 1.5cm substrate of quartz plate or Si wafer with concentrations ranging from 2wt to 5wt % of PAN solution. Formation of porous structure was achieved by a thermal imprinting technique in a vacuum oven at 250°C for 1.5h. After cooled down at room temperature for 10min, the soft mold was detached from the PAN film with the substrate. Subsequently, the carbonization of patterned PAN film was conducted as the method which made flat carbon film. Whole procedure was shown in Figure 3.

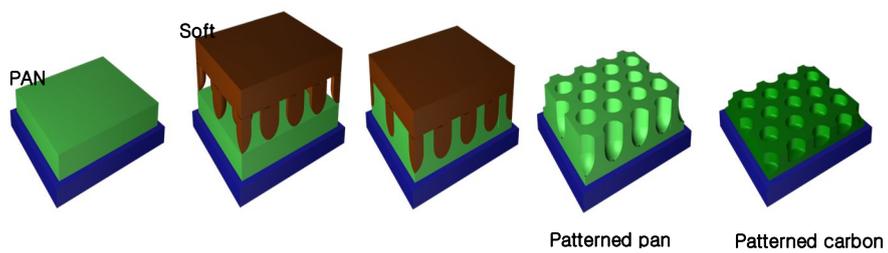


Figure 3. Schematic route to fabricate hexagonally patterned carbon film via thermal imprint

## 2.3 characterizations

An interferometer (filmetrics, F20-UV) was used to measure the thickness of the PAN film. Roughness of the flat carbon film and morphology of the patterned carbon film was measured by an atomic force microscopy (AFM, SII NanoTechnology, Inc. SPA-300HV). Furthermore, the structure of the master mold and the soft mold was investigated by scanning electron microscope (SEM, JSM-6701F, JEOL). The carbon film thickness was obtained by AFM, however, in carbon film formed from dilution solution (1~2 wt%) was investigated by XRR (PANalytical B.V.X'pert Pro) with a Cu K $\alpha$  radiation at 40keV and 30mA. The structure of the carbon film was checked by a synchrotron radiation facility, 4C or 9A beamline of Pohang Light Source (PLS\_II, Pohang, Republic of Korea, bending magnet type, critical energy : 10keV at 3.0GeV). Moreover, Raman spectrometer (Renishaw, in via Raman Microscope) was used to characterize the structure of the carbon film at a wavelength 514nm. The optical properties of the flat carbon film and the patterned carbon film were measured in reflectance and transmittance using the interferometer

and UV-vis spectrometer (Perkin-Elmer, Lambda 20). A 4-point probe was used to measure the electrical properties of both samples. Schematic diagram of XRD instrument was shown in figure 4.

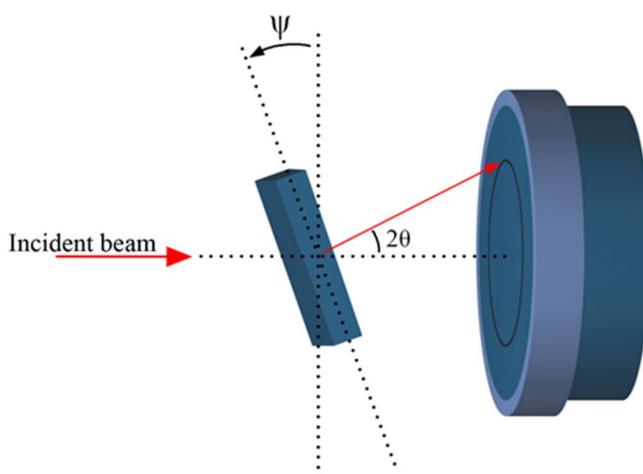


Figure 4. Schematic diagram of XRD instrument [24]

## 3. Results and discussion

### 3.1 Preparation of PAN film

Spin-coating was carried out to prepare the PAN film. It is important to get uniform PAN film because this affects quality of final product. However, it is generally a difficult task to achieve uniform PAN film from spin-coating, because of poor solubility of the PAN in a solvent. Also, this low solubility can cause nuclei-formation in the solution, which leads its rough surface. Aside from that, quality of PAN film relies on the temperature, the humidity, and the spin speed. Since especially DMF used as a solvent in this study had the property sensitive to humidity, it is hard to get smooth PAN film. In order to solve these problem, PAN solution was prepared at high temperature ( $\sim 95^{\circ}\text{C}$ ). Then PAN film was spin cast on silicon substrate or the quartz at above 3000rpm. As it was not sufficient to prepare hot PAN solution for uniform PAN film, either laboratory controlled the humidity perfectly or spin-coater with a gadget to manipulate the humidity should be needed. The thickness of the PAN film was indicated in Table 2. Bulk PAN is crystalline polymer, however, in

order to investigate whether spin-coated PAN film is also crystalline, XRD experiment of PAN film (1, 2, and 5wt% PAN solution) was conducted. (Figure 5) The result showed crystalline one peak and broad amorphous halo, which indicates PAN film is crystalline polymer. [24]

Concentration of PAN solution (wt%)	Thickness (nm)
2	53
3	110
4	200
5	270
6	376
7	573

Table 2. Thickness of PAN film according to concentration

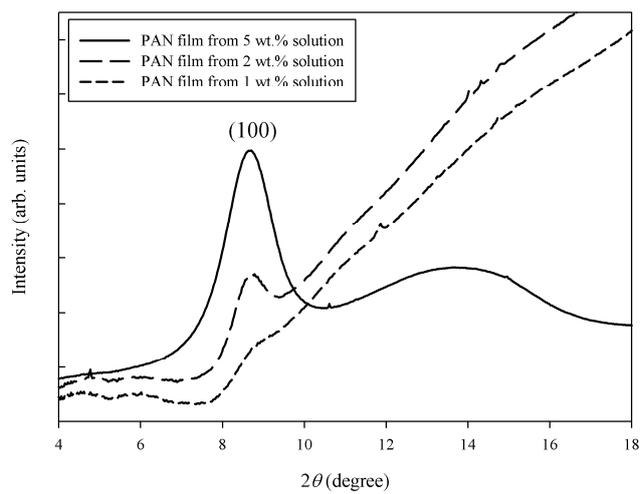


Figure 5. XRD of PAN films from 1, 2, and 5 wt% PAN solution [24]

## 3.2 Preparation of Carbon film

### 3.2.1 Pre-heat treatment

Pre-heat treatment is a process of formation of the poly-imine ladder polymer which become a carbon precursor. A subsequent oxidative process (carbonization) of the poly-imine ladder polymer produces an aromatized ladder structure, as its shape keeps during the process at high temperature. [14] The stabilization was carried out in both air and vacuum, though generally done in air.[14,25] Roughness of these samples was measured by AFM, shown in Figure 6. The carbon films prepared under both conditions had relative uniform surface without large cracks or defects. However, the sample stabilized in vacuum had smoother surface than the sample stabilized in air. While the root mean squared average roughness ( $R_s$ ) of the carbon film stabilized under vacuum was only 4.4nm for the 100nm thick film,  $R_s$  of the one stabilized in air was about 15nm. Vacuum condition was choosed as condition of the pre-heat treatment in this study. There are possible explanations of the results. First, during the stabilization under vacuum, removing residual or impurities could be one of the reason. Secondly, Oxidative behavior in crystalline polymer is quite different from other

polymer. That is because movement of oxygen in amorphous area is faster than in crystalline region. This variance cause difference of the sample's uniformity according to the stabilization condition. There were studies about difference of quality of these samples based on stabilization process between under air and under inert gas atmosphere.

[24, 26-27]

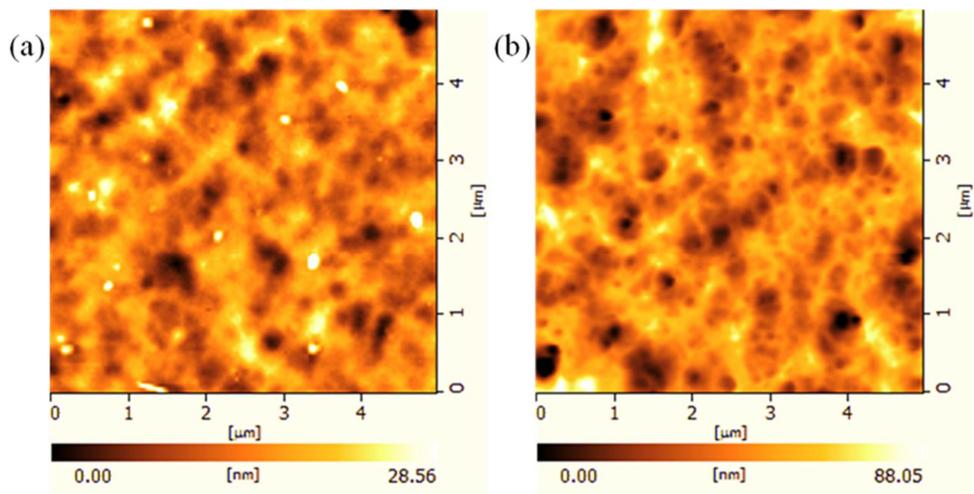


Figure 6. AFM roughness measurement of carbon film stabilized (a) in vacuum and (b) in air [24]

### 3.2.2 Carbon film structure analysis

Thickness of the carbon film was measured by AFM, as a method measuring difference between carbon surface and exposed dent by scratching using a sharp tool, shown in Figure 7. While it was difficult to measure thin carbon film below 10nm through the technique, these samples were measured by XRR to get more precise results and to approve whether AFM measures the thickness precisely. The thickness of carbon film from PAN solution (2wt, 5wt) using XRR was shown in Figure 8. After angle (x axis) of XRR data was transformed into  $q$ , where  $\lambda$  is 0.15418nm.

$$q = \frac{4\pi}{\lambda} \times \sin \theta$$

, calculating the thickness using  $t \approx 2\pi / \Delta q$  from  $q$  and Bragg's law,

$$\lambda = 2t \sin \theta$$

The whole results from the AFM was indicated in Figure 9. Compared to the thickness of the PAN film and the carbon film, thickness of the carbon sample was largely depressed because of changing structure and shrinkage by removed small atoms in the ladder polymer. [24] Also, there were studies about polymer weight loss during the carbonization

process of PAN. [28] The structure of the carbon film was investigated by X-ray Diffraction (XRD) and Raman spectroscopy. The XRD analysis of the carbon sample from PAN 5wt% solution was conducted as changing rotating angle  $\psi$ . In Figure 10, there were only one weak diffraction ring and amorphous halo around it. It was implied that the carbon film has low degree of crystallinity. In Figure 11, circular average 1-dimensional plot indicated obvious peak at about  $2\theta = 10.9^\circ$ . D-spacing was 0.356nm calculating using the Bragg's law for  $2\theta = 10.9^\circ$ , which matched with the reflection of (002) plane of hexagonal carbon structure. However, (100), (101) reflection were not observed because of limit of measure for large  $2\theta$ . Stacking height of layer plane ( $L_c$ ) was 0.722nm which was calculated value using full width at half maximum (FWHM) with Scherrer equation with shape factor 0.91. As increasing  $\psi$ , the XRD pattern did not change, which meant there was no specific orientation. The film thickness used in XRD experiment was about 100nm which was too thick to effect the XRD pattern. Unfortunately, the apparent XRD pattern of the carbon film containing thickness 4nm was not observed for the reason of lack of amount of medium. Furthermore, Raman spectroscopy measurement was carried out to check the structure of the carbon film, shown in Figure 12. The spectra for the carbon film indicated two peaks and one broad peak which were D, G, and 2D bands. Compared to the

other carbon materials, the result meant that the carbon film had a lack of spatial uniformity. [24]

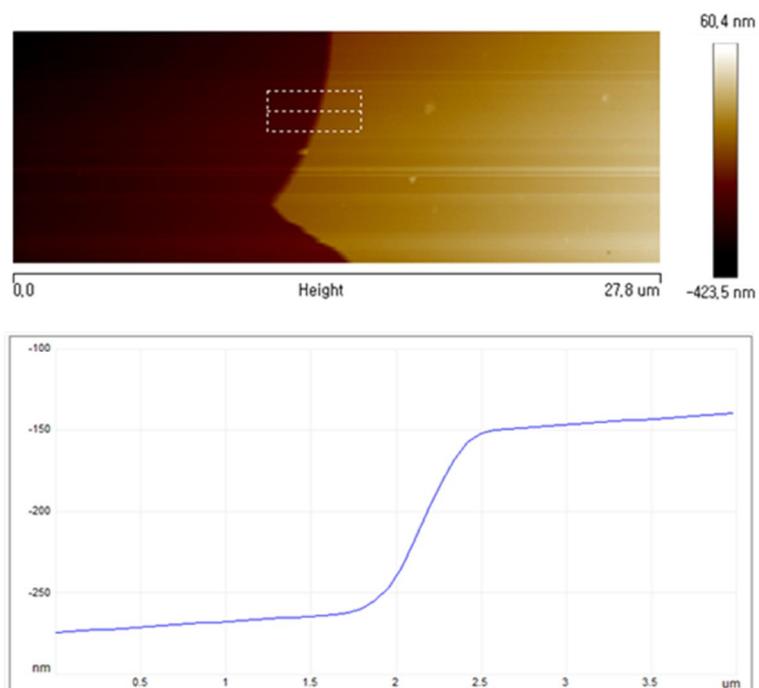


Figure 7. AFM thickness measurement of carbon film (5 wt% PAN

solution) [24]

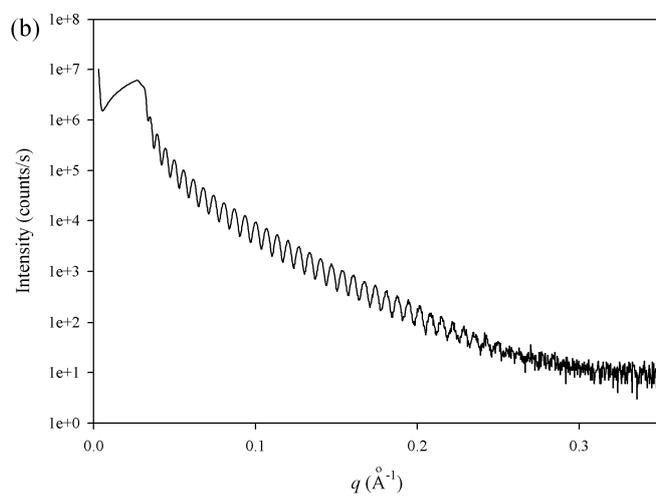
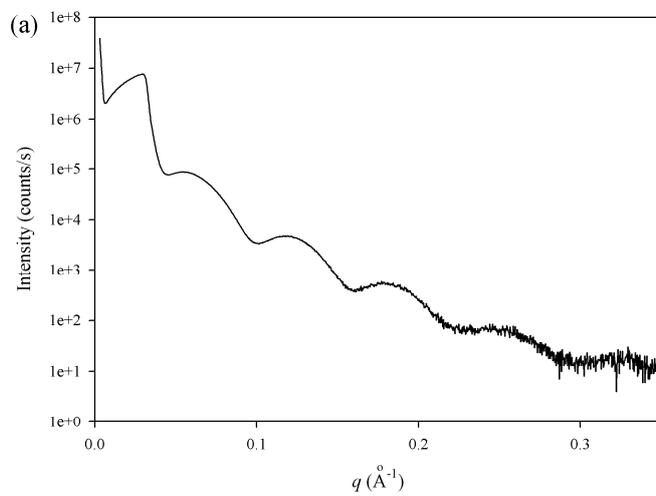


Figure 8. XRR of carbon films from (a) 5wt % (b) 2wt % PAN solution [24]

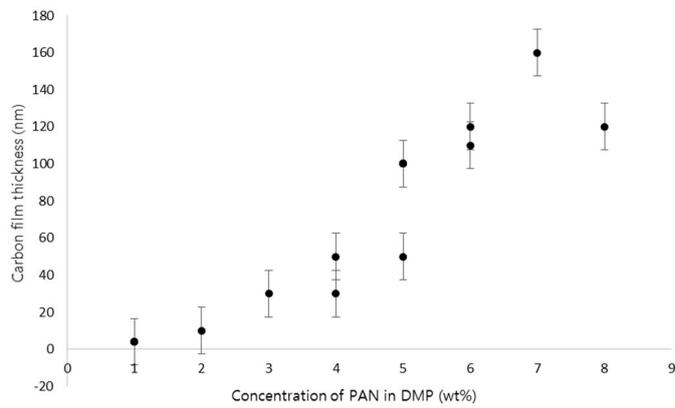
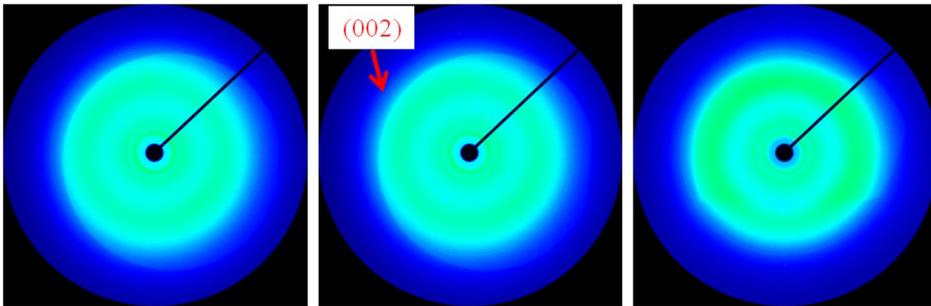


Figure 9. Thickness of carbon film according to variety concentration of PAN solution



$\Psi = 0^\circ$

$\Psi = 20^\circ$

$\Psi = 60^\circ$

Figure 10. XRD patterns of flat carbon film from 5 wt% PAN solution at different angle (2-D patterns) [24]

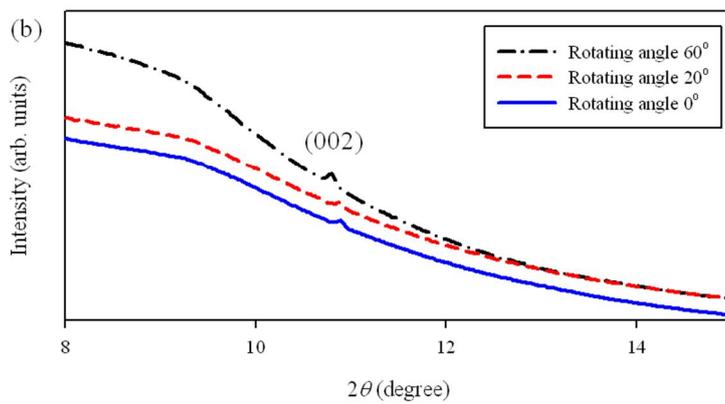


Figure 11. XRD patterns of flat carbon film from 5 wt% PAN solution at different angle (circular average 1-D plots in 2-D patterns) [24]

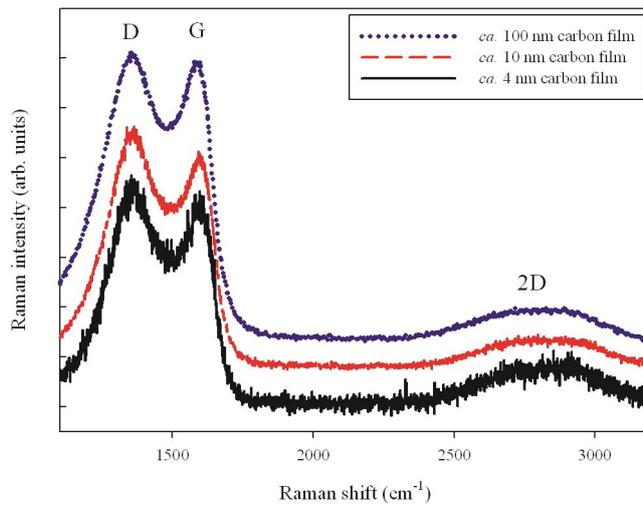


Figure 12.

spectra

carbon

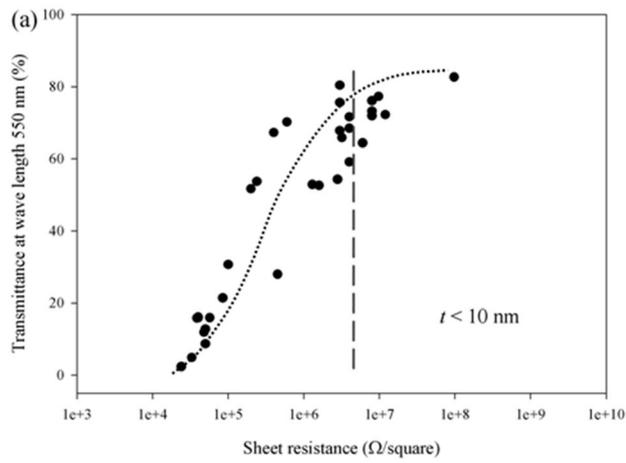
thickness 100nm, 10nm and 4nm [24]

Raman  
of  
films for

### 3.2.3 Optical and electrical properties analysis

Prepared the carbon film was expected to be the transparent electrode such as pixel electrode. The transparent electrode should be satisfied with sheet resistance ( $500 \Omega/\text{sq}$ ) and transmittance (85 %) at the same time. The carbon film was investigated about optical and electrical properties to approve whether to apply as transparent electrode, shown in Figure 13, 14. Looked into the results precisely, as increasing the sheet resistance, transmittance and reflectance was augmented. Also, the optical values versus the electrical information was saturated to a point, where had sheet resistance about  $10^6 \Omega/\text{sq}$  and thickness about 10nm. Unfortunately, the carbon film did not achieved the performance of the transparent electrode.

Figure 13.



Plot of

transmittance versus sheet resistance of flat carbon film at wave length 550 nm [24]

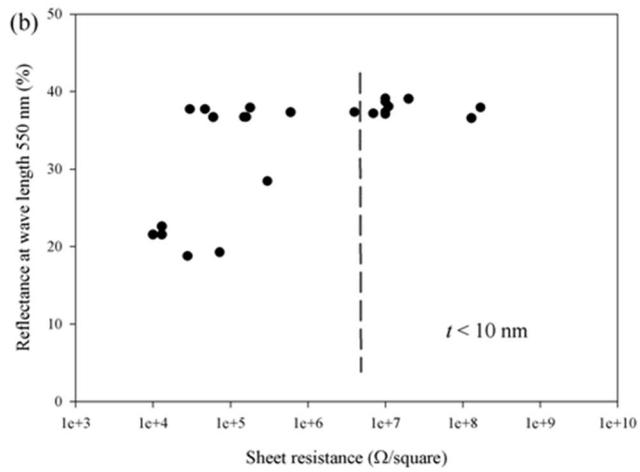


Figure 14. Plot of reflectance versus sheet resistance of flat carbon film at wave length 550 nm [24]

### 3.3 Preparation of patterned carbon film

### 3.3.1 AAO master mold, soft mold

Well-ordered porous structure of the master mold was achieved by two step anodization.[23] This morphology was shown in Figure 15. The AAO size was determined depending on the electrolyte, applied voltage, and second anodization time etc. The experiment were conducted in oxalic acid, 40V at 15C°, achieving the 30nm of the pore diameter, the 110nm of pores center to center distance. The second anodization was carried out for 1min, acquiring the 80nm of pore length. In addition, Pore-widening in phosphoric acid at 30° was done to enlarge the pore diameter, getting the 80nm of pore diameter. The master mold was chemically modified to give anti-adhesion property easy to detach the soft mold from it. The soft mold was prepared using the uv-curable polymer, shown Figure 16. As the soft mold was reused in the imprinting technique as the stamp, it had strong point economically. The pore diameter and length of the soft mold was c.a. 80nm and 80nm, respectively.

### 3.3.2 Patterned carbon film morphology

As mentioned before, patterning was introduced in order to increase the performance of the carbon film. Especially, the transmittance was expected to increase through the patterning of the carbon film.

Although PAN as a resin is thermoplastic, it is semi-crystalline polymer not to melt on mild conditions. In patterning of semi-crystalline polymer, while amorphous region is well-patterned, crystallite region is not patterned. So, in spite of the temperature above glass transition, it is required to raise the temperature until the crystallite region flows. The  $T_m$  and  $T_g$  of PAN is  $80^\circ\text{C}$  and  $317^\circ\text{C}$ , respectively. The optimum operating temperature was found through reiteration experiment,  $250^\circ\text{C}$ . The PAN films on the silicon and the quartz substrate was carried out by the thermal imprinting using the PU-based soft mold prepared at  $250^\circ\text{C}$  in vacuum for 1h 30min. Although it is successful to imprint the pattern, the depth of the pattern was smaller than that of the master mold. Pattern height of patterned PAN film from 5wt is only 16nm and pattern height of the one from 2wt is 11nm with pore size c.a. 80nm. And then subsequent two step carbonization of the patterned PAN film was done in the same procedure as flat carbon film. The AFM images of the patterned PAN film (2wt, 5wt PAN solution) and its carbonized film was shown in Figure 17, 18.

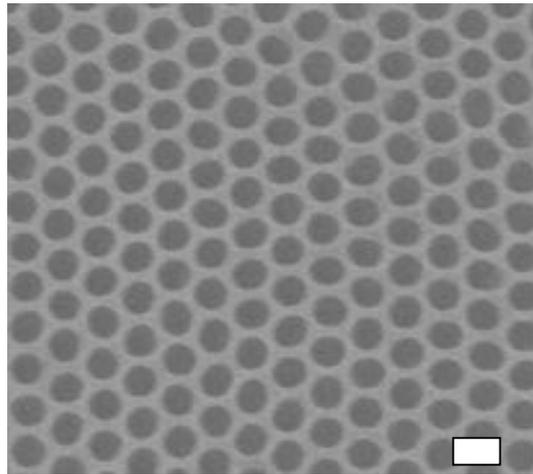


Figure 15. SEM image of top view of master mold (bar : 100nm)

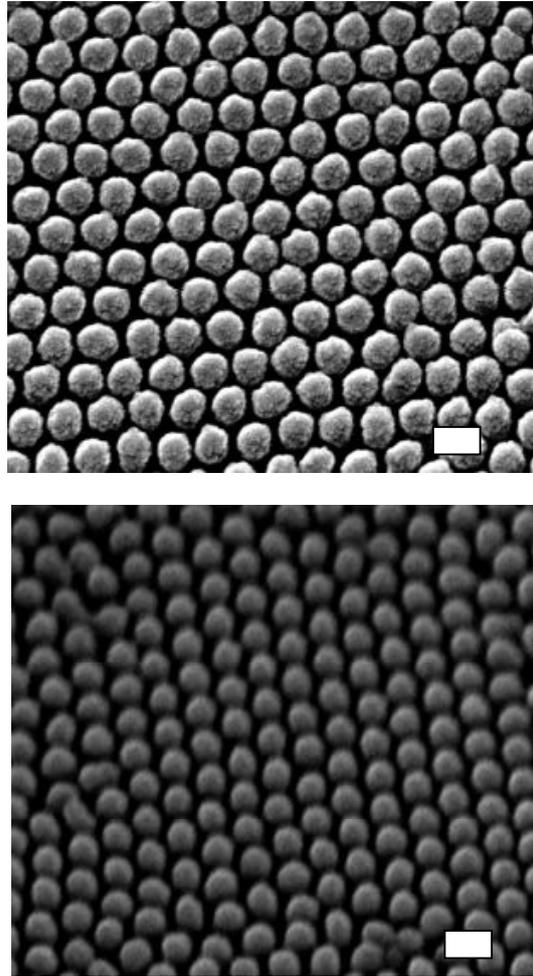


Figure 16. SEM images of top view and 45° tilted view of soft mold  
(bar : 100nm)

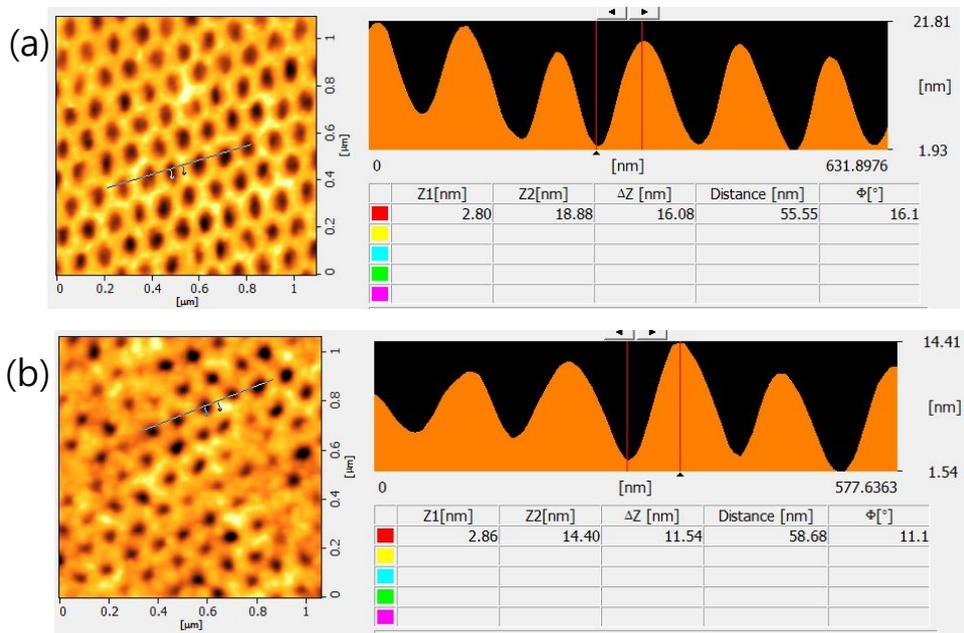


Figure 17. AFM images of patterned PAN film from (a) 5wt, (b) 2wt PAN solution

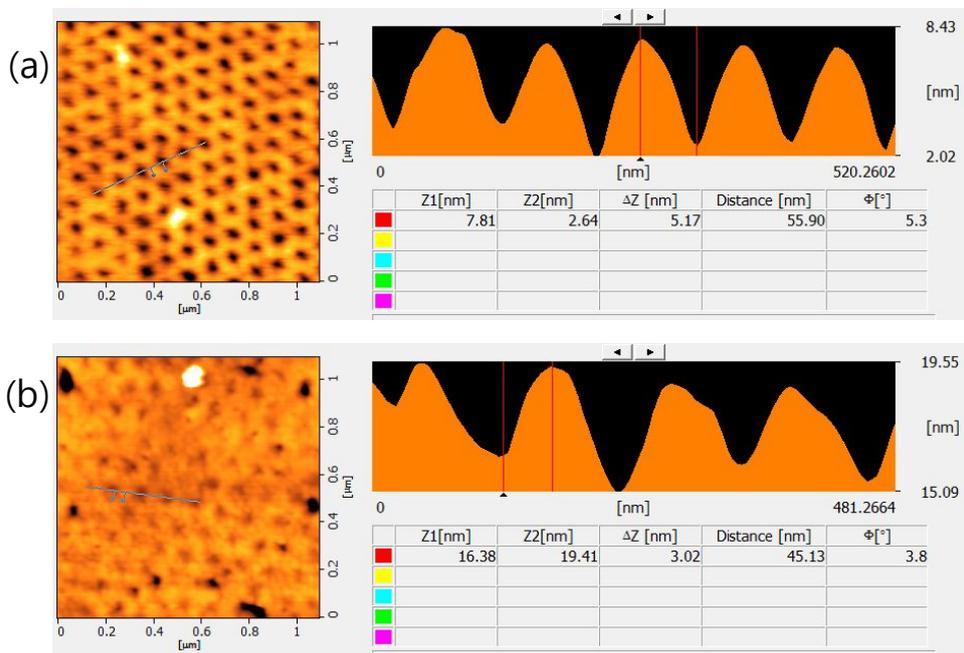


Figure 18. AFM images of patterned carbon film from (a) 5wt%, (b) 2wt% PAN solution

### 3.3.3 Optical and electrical properties analysis

The optical and electrical characteristics of the porous patterned carbon film was investigated and compared with the results of the flat carbon film, shown Figure 19,20. As the electrical properties rose up, transmittance and reflectance also increased. Aside from the expectation, patterning did not affect augment of the transmittance largely and the results follow the trends of the flat carbon film. One of the possible reasons for not showing large change from the trends is that increasing effects of the optical properties by patterning was compromised with increment of the resistance. Another possible reason is that dimension of the pattern of the sample is too small to affect the optical properties. As the light source of a device measuring optical property has wavelength a few hundreds nanometer scale, the nanoscopic pattern below 100nm cannot affect the optical properties.

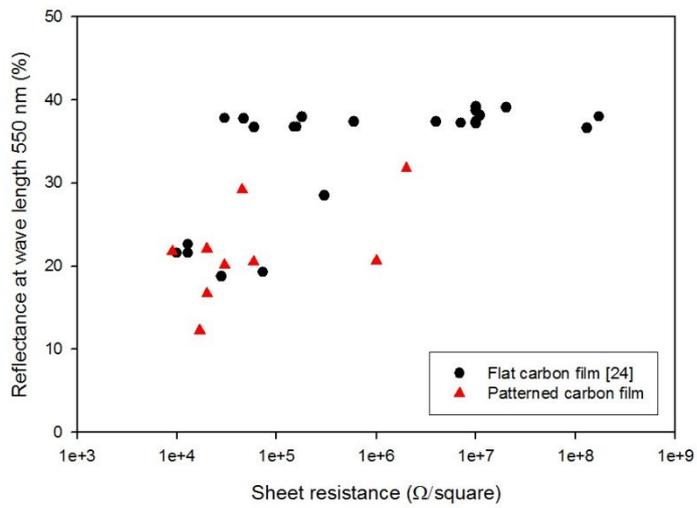


Figure 19. Plot of reflectance versus sheet resistance of patterned carbon film with flat carbon film at wave length 550 nm

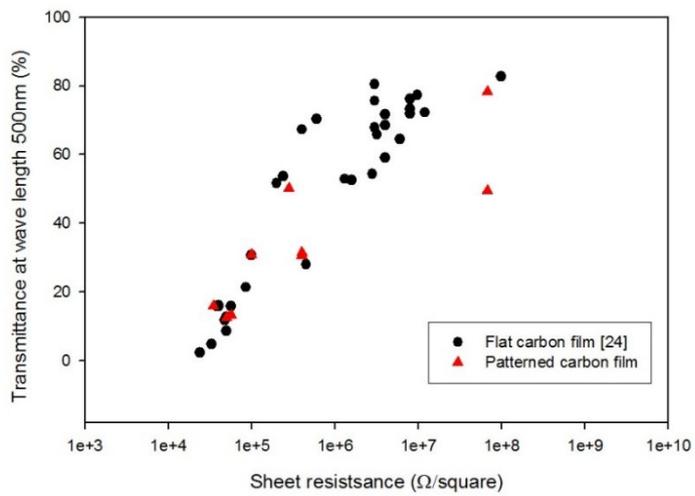


Figure 20. Plot of transmittance versus resistance of patterned carbon film with flat carbon film at wavelength 550 nm

## 4. Conclusions

Ultrathin carbon films from spin-coated polyacrylonitrile film were achieved by the carbonization. This permitted the production of large, conductive films through a simple manner on comparatively mild operation conditions. The uniform PAN film was achieved by spincoating and its structure and thickness were investigated. The PAN film showed semicrystalline polymer which was same as bulk PAN. The carbon films were investigated the structure, optical and electrical properties. The sample stabilized under vacuum had smoother surface than one stabilized under air, however, both samples presented continuous carbon layer without large defects. The carbon film showed low crystallinity with weak diffraction pattern from (002) reflection and large amorphous halo. There was not specific orientation for the carbon films with thickness 100nm because of relatively large magnitude. Concerning the relation of optical and electrical values, the film sheet resistance was saturated to c.a.  $10^6 \Omega/\text{square}$  at c.a. 10nm of the film thickness. Furthermore, patterned carbon film was prepared through the imprinting. The AAO mold was used as the master mold. As a result, nano porous shape was achieved. The imprinting method using the AAO allows for attaining patterned samples in cost efficiently and easily, compared to

conventional patterning method such as photolithography. Since the soft mold was modified chemically for anti-adhesive properties, it is acceptable to reuse the soft mold, which attracts the researchers from economic point of view. Similar to the flat carbon films, optical properties of the patterned carbon films according to the resistance were investigated. Although the transmittance and the reflectance of these films increase against augment of the resistance, did not deviated from trends for the flat carbon films. This is because augment of the transmittance was trade-off by increasing the resistance. This study was showed possibility of the application of the carbon film to the transparent electrode, especially the pixel electrode, though the sample was not sufficient to meet the performance of the transparent electrode.

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## 국문 초록

디스플레이 산업에서 Indium Tin Oxide (ITO) 는 우수한 전기적, 광학적 성질 때문에 투명전극으로 많이 사용되어 왔다. 하지만, 지구상의 ITO가 고갈 되어져 가고 ITO에 외력이 가해졌을 때, 부서지기 쉬운 성질을 갖고 있어 flexible 디스플레이에 적용하기 어려운 단점을 가지고 있어서 ITO를 대체할 물질들이 많이 개발되어 오고 있다., 특히 좋은 전기적 화학적 성질이 장점인 탄소 물질이 각광받고 있다. 이 연구에서는 스피코팅으로 얻어진 Polyacrylonitrile (PAN) 박막을 두 단계의 탄소화 과정 (stabilization, further oxidation)을 통해 탄소박막을 만들었다. PAN을 전구체로 사용한 이유는 상대적으로 낮은 온도에서의 Pre-heat treatment을 통해 탄소화 과정에 필요한 Poly imine ladder polymer를 만들 수 있는 이점이 있기 때문이다. 만들어진 탄소전극의 구조, 전기적 광학적 성질 관계, 정성적 성질 등이 조사되었다. 또한 stabilization과정을 공기상태와 진공상태의 두 조건에서 모두 시행 하여 더 나아가 탄소화를 거치고 난 뒤 어떠한 특성 차이가 있는지도 조사되었다.

탄소전극의 광학적 성능을 향상 시키기 위해 패터닝 기술을 도입하였다.

두 단계 양극산화공정을 통해 얻어진 AAO를 마스터 몰드로 사용하였고, 마스터 몰드의 화학적 표면처리 후, UV경화가 가능한 Polyurethane계열의 고분자를 이용해 마스터몰드의 역 구조를 얻어, 소프트 몰드를 준비하여 이용했다. 이 소프트 몰드도 마스터 몰드와 같이 접착방지막을 형성시키기 위해 화학적 표면처리를 한 후, 이 소프트 몰드를 스탬프로 스피코팅 된 PAN 박막 위에 나노 임프린팅을 수행하고 앞서와 같이 두 단계의 탄소화를 통해 기공구조의 패턴을 가지는 탄소전극을 만들었다. 이 패턴 된 탄소전극의 형태와 전기적, 광학적 관계를 조사하였다. PAN이 semicrystalline polymer라서 다른 PMMA나 PS 등의 나노 임프린팅 보다 더 높은 온도에서 진행이 되었지만, 흐름성이 좋은 고분자들 보다 얇은 패턴이 달성 되었다. 패턴이 되지 않은 탄소전극과 광학적 특성 면에서 별 다른 차이를 보이지 않았다. 불행하게도, 시중에 쓰이는 투명전극만큼의 성능을 도달하지 못했지만, 간단한 공정을 통해 탄소전극을 만들고 패턴이 있는 탄소전극을 달성하여 탄소물질이나 유기 투명전극물질의 연구에 큰 도움이 될 수 있다.

