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Fabrication of metallic nanomesh structures using phase shift lithography and its application to touch screen panels

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ABSTRACT

This study reports on the fabrication process of a nanomesh-shaped nickel mold by using phase shift lithography. We also present its application to a transparent electrode film for a touch screen panel. A suitable gap between the checkerboard- shaped patterns on a photomask was chosen to obtain the nickel mold with a mesh-shaped pattern connected to each other. A nanomesh-type trench pattern was transferred from the nickel mold onto a polyethylene terephthalate film through the imprinting lithography process with ultraviolet light. The nanomesh- embedded electrode pattern was fabricated by filling the nanotrench with Ag paste. The light transmittance and sheet and line resistance of the nanomesh-type transparent conducting electrode film were evaluated. The TCE film was then applied to a 7 in. touch sensor module.

1. Introduction

Transparent conducting electrodes (TCE) are a key component in many optoelectronic devices, including photovoltaics (Granqvist, 2007), organic light-emitting diode (OLED) (Gu et al., 1996), and touch screen panels (TSP) (Bae et al., 2010). Currently, indium tin oxide (ITO) is widely used as an electrode material because of its high optoelectronic performance. However, the brittleness of ITO (Chen et al., 2001) increases the need for substitutional materials, such as carbon nanotube, graphene, metal mesh, and random networks of metallic nanowires (Gaynor et al., 2011). The capacitive-type TSP of a large-area particularly requires a transparent electrode with a much lower sheet resistance, without decreasing the transmittance to achieve multi-tasking and multi-touch function with high quality. Thus, bodies of researches on the metal-mesh-based TCE film have been actively performed in the field of touch panel industry.

The two types of metal-mesh-based TCE film are the protruded and embedded patterns. On the one hand, the protruded pattern is made on the polymer substrate through the printing (Choi et al., 2015a, 2015b), lift-off (Kim et al., 2015), and etching processes (Hautcoeur et al., 2011), among others. On the other hand, the embedded pattern can be fabricated by filling the trench structures on the flexible substrate with electrode material (Chen et al., 2012). The embedded mesh pattern on the flexible substrate (e.g., polyethylene terephthalate (PET) film) may generally cause a better adhesion than the protruded mesh pattern because the metallic pattern deposited on the polymer substrate is likely attacked by humid air, which is passed through the polymer substrate (Choi et al., 2015a,b). In addition, the embedded pattern, which successfully filled the trenches with a high aspect ratio, may be formed thicker than the protruding pattern. Consequently, the TCE film with an electrode embedded in the trench pattern with a high aspect ratio has a lower sheet resistance at a given light transmittance (van de Wiel et al., 2013).

(Yu et al., 2013) fabricated the embedded micromesh-type TCE film with superior transparency and sheet resistance compared to the conventional ITO films. However, appearance problems, such as the moiré phenomena and the pattern visibility issue, must be solved so that the micromesh-shaped transparent electrodes can be applied to the TSP (Shin and Park, 2015). One of the best methods to solve these TSP problems is the use of nanomesh for the TCE film.

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We report herein on the fabrication process of metallic nanomesh structures by using phase shift lithography. We then present its application to a transparent electrode film for a touch screen panel. The nickel mold was prepared through the phase shift lithography (Rogers et al., 1997) and electroforming processes (Kim and Mentone, 2006). A nanomesh-type trench pattern was transferred from the nickel mold onto a PET film through the imprinting lithography process with ultraviolet (UV) light. The nanomesh-embedded electrode pattern was then fabricated by filling the nanotrench with Ag paste. The TCE film, on which the Ag paste-based nanomesh pattern was embedded, was then finally applied to the 7 in. TSP module.

2. Experimental details

2.1. Nickel mold preparation

We fabricated the nickel mold to form a nanotrench pattern on the PET film through the phase shift lithography process. The process has the advantage of quickly and economically fabricating a nanopattern on a large area using a phase mask with UV light. Kwak et al. (2012) stated that the nanomesh pattern can be fabricated through the phase shift lithography with a specially designed elastomeric phase mask.

Fig. 1 shows a schematic illustration of the fabrication process of the nickel mold that formed a nanotrench pattern. First, a photomask (Cr mask) with a checkerboard-shaped pattern was placed on a substrate to prepare the master pattern for the phase mask. A positive tone photoresist (AZ GXR 601, AZ Electronic Materials) was coated in 2 μm thickness on the substrate, and baked at 110 °C for 1 min (Fig. 1(a)). A UV exposure with an intensity of 30 mJ/cm^2 was then performed. Subsequently, the photoresist was developed for 90 s in a 300MIF developer (AZ Electronic Materials). Fig. 1(b) shows that the checkerboard-shaped pattern can be fabricated on the glass substrate.

An elastomeric phase mask was then fabricated from the master pattern. For the phase shift lithography process, the air gap between the phase mask and the photoresist provided a significant effect on the pattern line width because the light intensity difference at the interface between the wall and the air region on

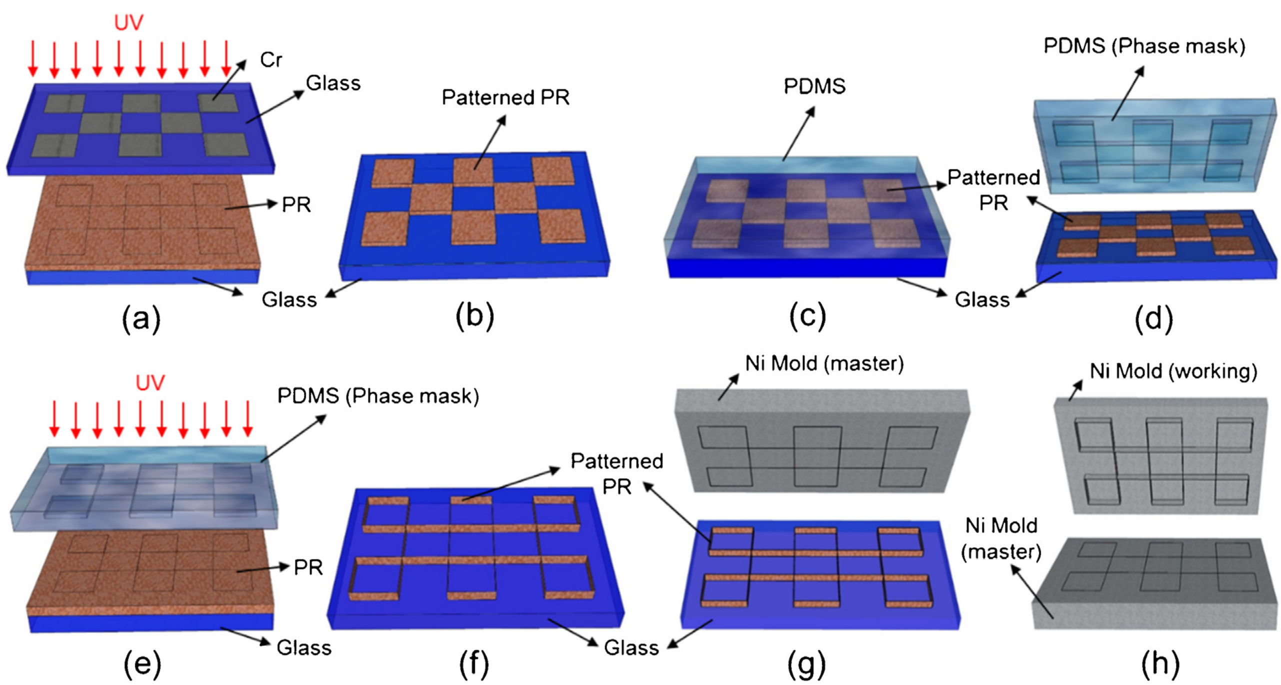

Fig. 1. Schematic illustration of the nickel mold fabrication process through phase shift lithography process: (a) photo lithography process with a conventional photomask (Cr mask), (b) master pattern for a phase mask, (c) PDMS pouring and curing process, (d) phase mask, (e) phase shift lithography process with a phase mask, (f) master pattern for a nickel mold, (g) master mold (mesh-shaped trench structure), and (h) working mold (mesh-shaped protruded structure).

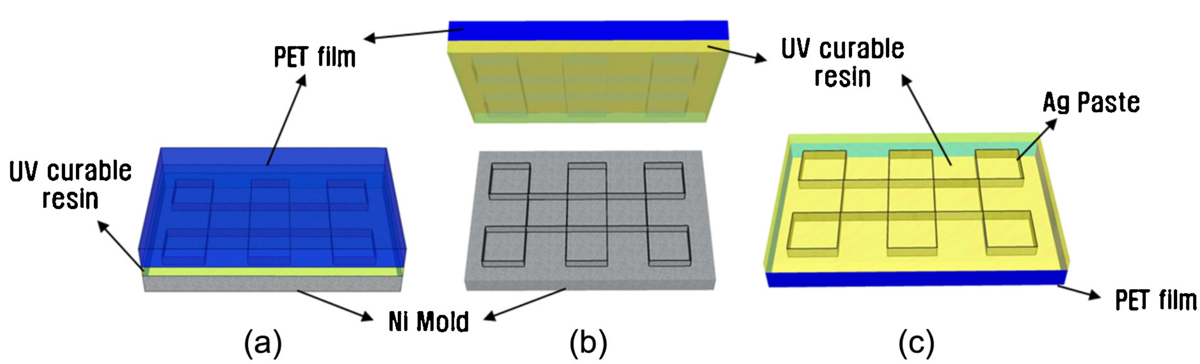

Fig. 2. Schematic illustration of the fabrication process of the Ag paste-based nanomesh electrode: (a) Pouring process of UV curable resin over a working mold, (b) Peeling off the nanotrench-patterned film and (c) the Ag paste filled TCE film.

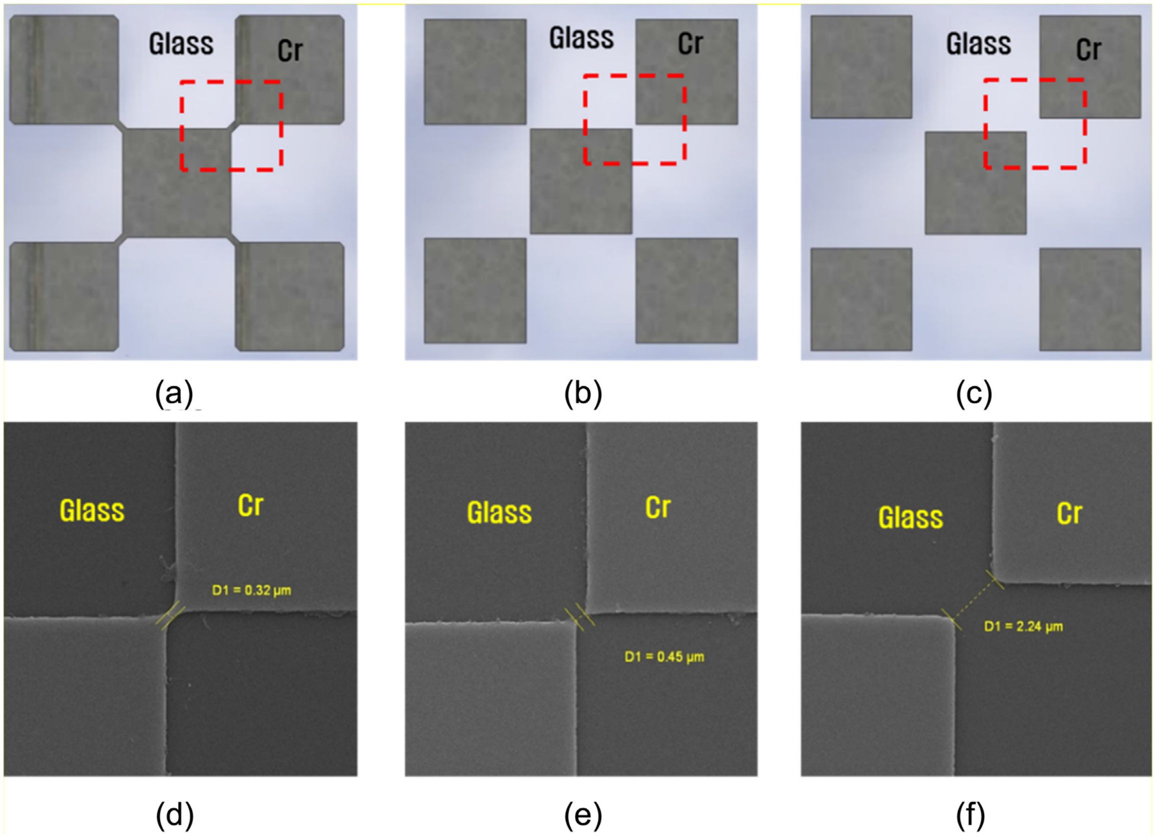

Fig. 3. Schematic diagrams and SEM images of the Cr patterns on a photomask: (a) photomask design with no gap, (b) photomask design with a suitable gap, (c) photomask design with a very wide gap, (d) SEM image without gap, (e) SEM image of a suitable gap, and (f) SEM image of a very wide gap.

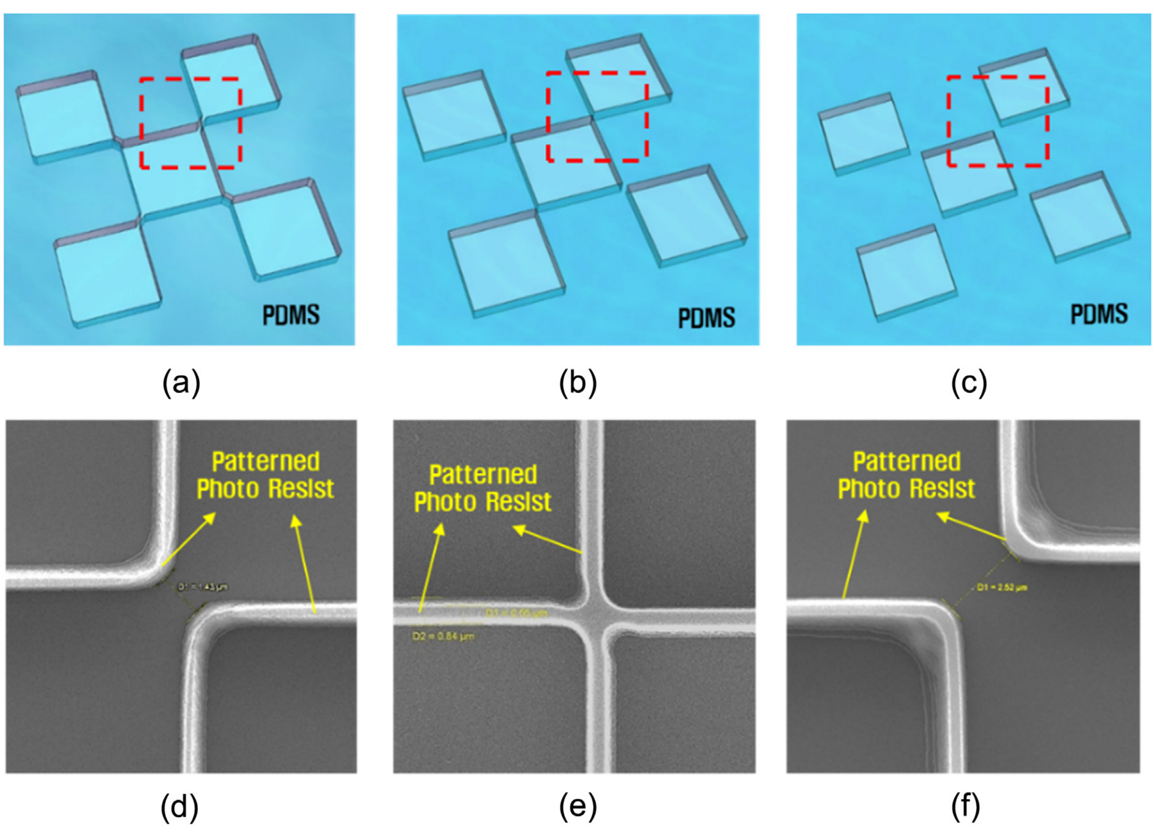

Fig. 4. Schematic diagrams of the original pattern on a phase mask and SEM images of the photoresist pattern generated through the phase-shift lithography process: (a) PDMS structures without a gap, (b) PDMS structures with a suitable gap, (c) PDMS structures with a very wide gap, (d) phase-shift lithography result with no gap phase mask, (e) phase-shift lithography result with a suitable gap phase mask and (f) phase-shift lithography result with a very wide gap phase mask.

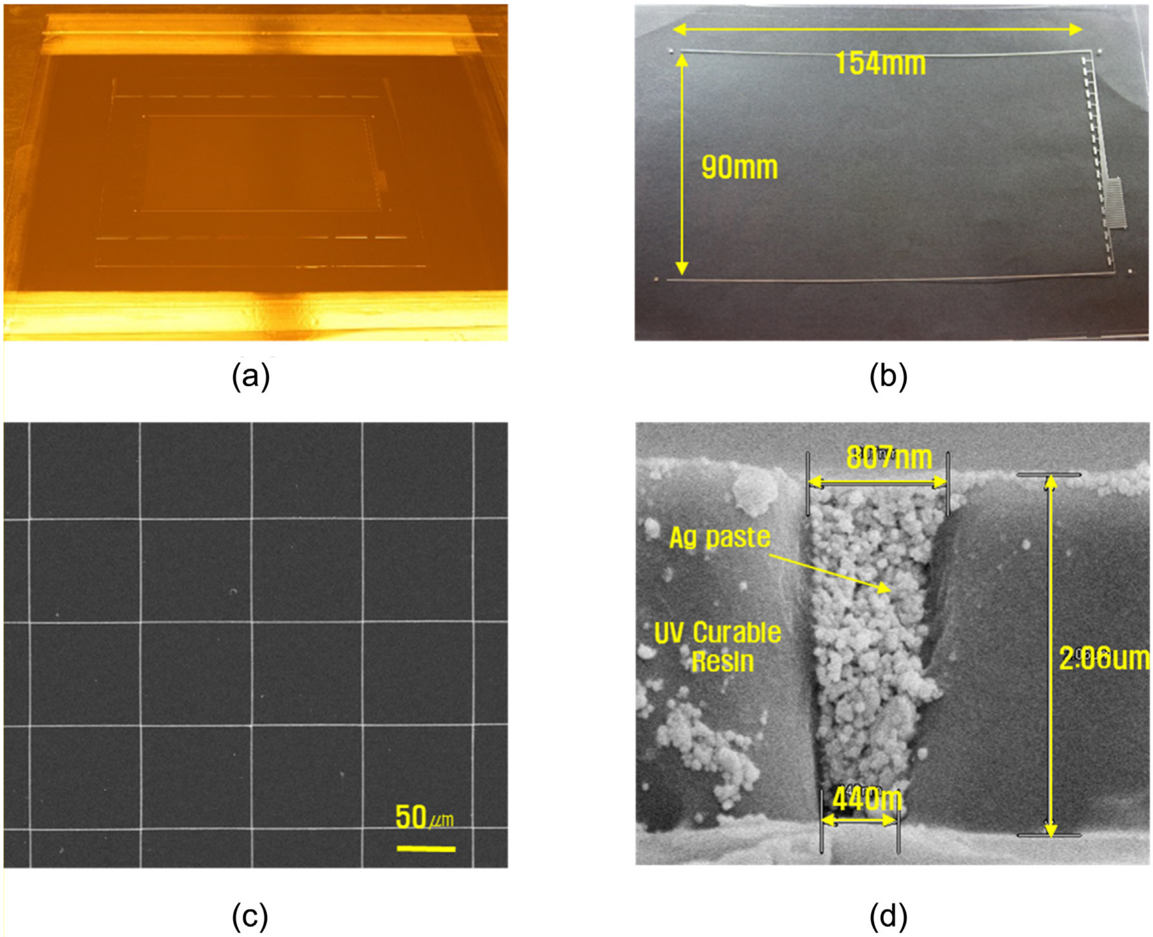

Fig. 5. Nickel mold and TCE films: (a) image of the nickel mold, (b) image of the TCE film, (c) SEM image of the TCE film (top-view), and (d) SEM image of the TCE film (cross-section-view).

the phase mask surface determined the pattern line width of the patterns. Eliminating the air gap between them was very difficult. Hence polydimethysiloxane (PDMS) was chosen as the soft transparent phase mask material herein. A PDMS pre-polymer (Sylgard 184, Dow Corning) was poured onto the photoresist pattern and cured at 80 °C for 1 h (Fig. 1(c)). The elastomeric phase mask was peeled off from the master pattern after thermal curing (Fig. 1(d)).

The phase shift lithography process was performed by coating a positive tone photoresist (AZ GXR 601, AZ Electronic Materials) on the glass substrate to a thickness of 2 μm and baking it at 110 °C for 1 min. The phase mask was placed in conformal contact to minimize the air gap between the phase mask and the photoresist (Fig. 1(e)). The UV light with an intensity of 40 mJ/cm^2 was then exposed on the photoresist layer. The photoresist was developed for about 1 min in the diluted 300 MIF developer (AZ Electronic Materials: 75 wt.% and DI water: 25 wt.%). The narrow photoresist pattern with a less than 1 μm width was produced along the outline of the original phase mask pattern after development process. The reason is the light intensity difference at the interface between the PDMS wall and the air region on the phase mask surface (Fig. 1(f)).

As a final step, the nickel stamp was fabricated from the master pattern through the electroforming process. A 20 nm thick Cr layer was deposited as a seed layer on the master pattern through the sputtering process. The electroforming process was performed to fabricate the nickel mold with 500 ± 25 μm thickness. An electroforming bath was maintained at around 50 °C and pH 4.5. The current density was 15–25 mA/cm^2. The deposition rate was 1–2 μm/min. The glass substrate, on which the photoresist patterns were fabricated, should be removed after the electroforming process. A part of the patterned photoresist and the deposited Cr layer remained inside the patterns on the first nickel stamp surface when the glass substrate was removed. The photoresist residue was dissolved by immersing in acetone. The Cr residue was removed through the wet etching process using a Cr etchant (Fig. 1(g)). As regards the seed layers, even though various metal materials (e.g., nickel, copper and titanium) can be applied, we chose the Cr seed layer considering the selectivity against the nickel material for the wet etching process.

The first nickel mold, which was a master mold, had mesh-shaped trench structures because it had the opposite shape of the photoresist pattern. The second nickel mold, which was a working mold, was then duplicated from the master mold through the electroforming process. The electroforming process for the second nickel stamp was performed under the same conditions in the first stamp fabrication after the Cr layer was deposited as the separation layer on the first nickel stamp surface. The first stamp was separated from the replicated nickel stamp after the electroforming process. The Cr residue was also removed through the wet etching process. Consequently, the protruding mesh pattern was fabricated on the working mold surface. The nanotrench pattern can possibly be formed on the flexible substrate (Fig. 1(h)).

2.2. Fabrication of the Ag paste-based nanomesh electrodes

Fig. 2 presents a schematic diagram of the fabrication process of the Ag paste-based nanomesh electrodes. The UV curable

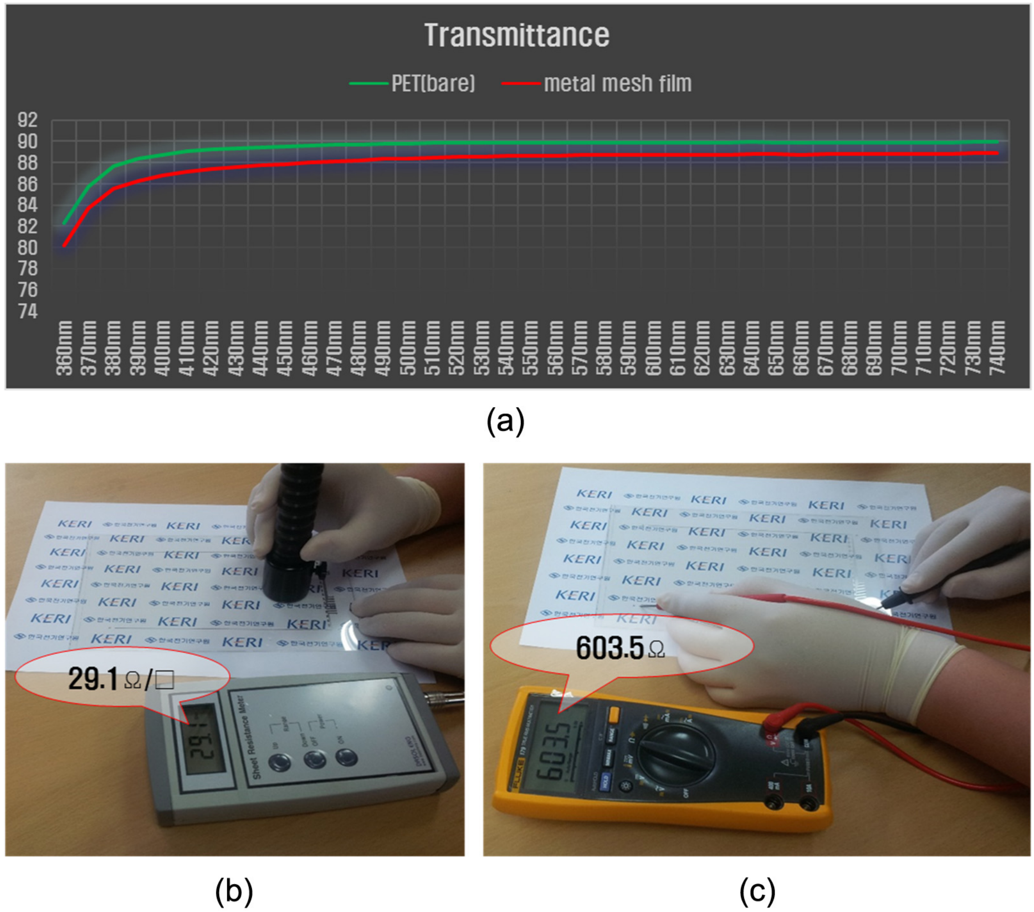

Fig. 6. Characteristics of the TCE film: (a) light transmittance, (b) sheet resistance, and (c) line resistance.

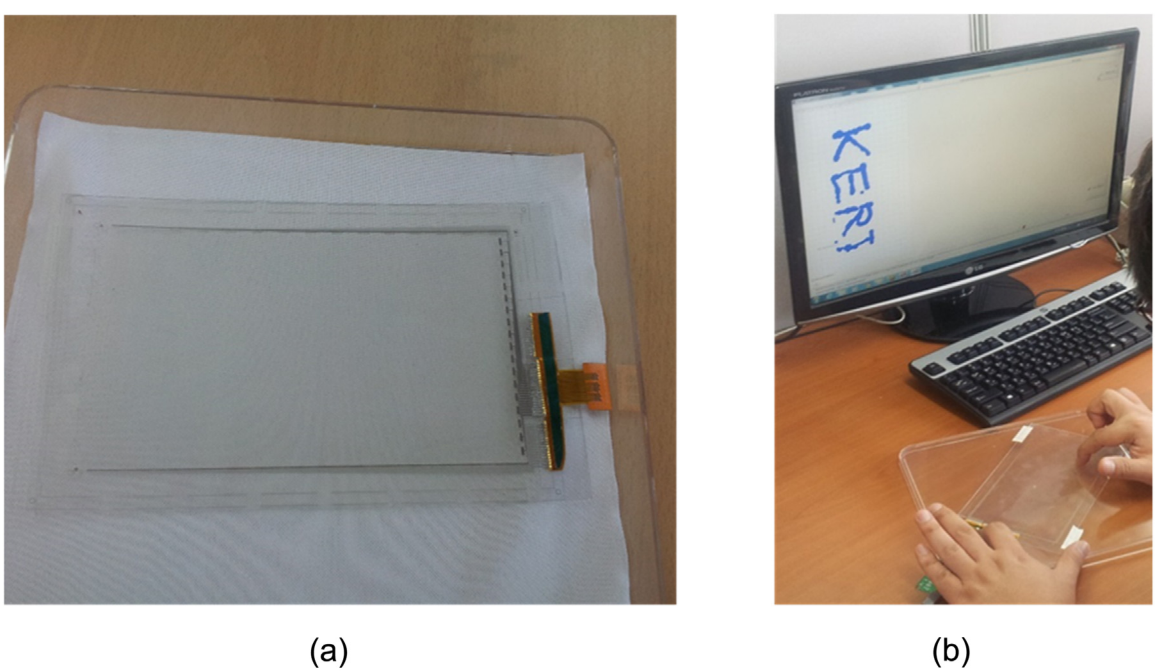

Fig. 7. 7 in. touch sensor module: (a) image and (b) operation of the touch sensor module.

polyurethane acrylate (MNR-03, Minuta Tech) pre-polymer was poured on the working mold surface. A supporting PET film was then carefully placed over the UV curable resin (Fig. 2(a)). Resin was cured by exposure to UV light in a dose of 600 mJ/cm^2. The nanotrench-patterned film was peeled off from the working mold after the UV curing process (Fig. 2(b)). The squeezing process was then performed to fill the mesh-shaped nanotrench pattern with Ag paste (TEC-PA-010, InkTec). A polyurethane squeezer was applied during the Ag paste filling process to avoid scratch on the nanotrench pattern of the UV curable resin. A PVA sponge was chosen as to perform the cleaning process of the Ag paste residues on the nanotrench patterns. The Ag paste-filled film was finally dried at 130 °C for 2 min in an oven (Fig. 2(c)).

3. Results and discussion

3.1. Nickel mold fabrication

Fig. 3 shows the images of the Cr patterns on the photomask used in this study. The photomask was commercially fabricated through the laser beam lithography and wet etching processes on the glass substrate. Three Cr patterns (i.e., none, none, 0.5 μm and 2.2 μm) were considered and tested with different gaps to evaluate the effect of the gap between two neighboring Cr squares on the results of the phase shift lithography process. Fig. 3(a)–(c) represent the schematic diagrams of the photomask designed for this study. Fig. 3(d)–(f) show the scanning electron microscope (SEM) images enlarged at two neighboring Cr squares.

The photomask was applied in preparing the phase mask through the photolithography and pattern transfer processes. Fig. 4 shows the appearance of the PDMS pattern and phase shift lithography results in the corresponding area to the photomask pattern in Fig. 3. Fig. 4(a)–(c) illustrate that the same pattern as the photomask was transferred on the phase mask surface. Among the three phase masks, only the phase mask with a suitable gap was able to generate the mesh-like photoresist pattern connected to each other (Fig. 4(e)). Meanwhile, the polymeric pattern of the mesh structures on the phase mask without a gap or with a very wide gap was disconnected to each other because the pattern was generated along only the contour of the original pattern on the phase mask (Fig. 4(d) and (f)). The 7 in. nickel mold herein is fabricated through the phase shifting lithography process with a phase mask pattern of a suitable gap.

3.2. Fabrication of the metal mesh electrode film for the TSP

The transparent electrodes for the herein were produced using the nickel mold, which is fabricated by the phase mask pattern of a suitable gap. Fig. 5(a) and (b) show the nickel mold image and TCE film, respectively. Fig. 5(c) and (d) represent the SEM images of the TCE film. The Ag paste-based mesh-type electrode had a width of several hundred nanometers and a pitch of 100 μm on the TCE film surface. Fig. 5(d) shows that the Ag paste has successfully filled the inside of the nanotrench.

Finally, 7 in. touch panel module was fabricated using the TCE film shown in Figs. 6 and 7(a) shows the 7in. touch sensor module and Fig. 7(b) demonstrates the fabricated touch sensor module operation.

4. Conclusion

We have presented a unique method of fabricating a nanomesh-shaped nickel mold for the transparent electrodes of touch screen panels. A suitable gap between the checkerboard-shaped patterns on a photomask was chosen to obtain the nickel mold with a mesh-shaped pattern connected to each other. The transparent conductive film, on which the Ag paste-based nanomesh pattern was embedded, was fabricated using the nickel mold. Accordingly, the light transmittance and sheet and line resistances were evaluated. The TCE film was finally applied to the 7 in. touch sensor module. The module was found to work successfully.

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References

Bae, S., Kim, H., Lee, Y., Xu, X., Park, J., Zheng, Y., Balakrishnan, J., Lei, T., Kim, H., Song, Y., Kim, Y., Kim, K., Ozyilmaz, B., Ahn, J., Hong, B., Lijima, S., 2010. Roll to roll production of 30-inch graphene films for transparent electrodes Nature. Nanotechnology 5, 574–578.

Chen, Z., Cotterell, B., Wang, W., Guenther, E., Chua, S., 2001. A mechanical assessment of flexible optoelectronic devices. Thin Solid Films 394, 202–206.

Chen, C., Hsieh, C., Ho, C., Sung, C., 2012. Insertion structures for transparent metal electrodes prepared by nanoimprint lithography. Appl. Phy. Exp. 5, 044202.

Choi, H., Choo, S., Jung, P., Shin, J., Kim, Y., Lee, H., 2015a. Uniformly embedded silver nanomesh as highly bendable transparent conducting electrode. Nanotechnology 26, 055305.

Choi, Y., Lee, E., Lee, T., Kim, K., 2015b. Optimization of a reverse-offset printing process and its application to a metal mesh touch screen sensor. Microelectron. Eng. 134, 1–6.

Gaynor, W., Burkhard, G.F., McGehee, M.D., Peumans, P., 2011. Smooth nanowire/polymer composite transparent electrodes. Adv. Mater. 23, 2905–2910.

Granqvist, C.G., 2007. Transparent conductors as solar energy materials: a panoramic review. Sol. Energy Mater. Sol. Cells 91, 1529–1598.

Gu, G., Bulovic, V., Burrows, P.E., Forrest, S.R., Thompson, M.E., 1996. Transparent organic light emitting devices. Appl. Phys. Lett. 68, 2006–2611.

Hautcoeur, J., Castel, X., Colombel, F., Benzerga, R., Himdi, M., Legeay, G., Motta-Cruz, E., 2011. Transparency and electrical properties of meshed metal films. Thin Solid Films 519, 3851–3858.

Kim, I., Mentone, P.F., 2006. Electroformed nickel stamper for light guide panel in LCD back light unit. Electrochim. Acta 52, 1805–1809.

Kim, B., Park, J., Hwang, Y., Park, J., 2015. Characteristics of silver meshes coated with carbon nanotubes via spray-coating and electrophoretic deposition for touch screen panels. Thin Solid Films, 68–71.

Kwak, M., Ok, J., Lee, J., Guo, L.J., 2012. Continuous phase-shift lithography with a roll-type mask and application to transparent conductor fabrication. Nanotechnology 23, 344008.

Rogers, J.A., Paul, K.E., Jackman, R.J., Whitesides, G.M., 1997. Using an elastomeric phase mask for sub-100 nm photolithography in the optical near field. Appl. Phys. Lett. 70 (20), 2658–2660.

Shin, D., Park, J., 2015. Design of moire-free metal meshes using ray tracing for touch screen panels. Displays 38, 9–19.

van de Wiel, H.J., Galagan, Y., van Lammeren, T.J., de Riet, J.F.J., Gilot, J., Nagelkerke, M.G.M., Lelieveld, R.H.C.A.T., Shanmugam, S., Pagudala, A., Hui, D., Groen, W.A., 2013. Roll-to-toll embedded conductive structures integrated into organic photovoltaic devices. Nanotechnology 24, 484014.

Yu, J., Jung, G., Jo, J., Kim, J., Kim, J., Kwak, S., 2013. Transparent conductive film with printable embedded pattern for organic solar cells Materials and Solar. Cells 109, 142–147.