Surface Modification of Thin Film using Trimethylchlorosilane Vaporization Treatment

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Keywords : surface modification, vapor treatment, trimethylchlorosilane, surface energy, self assembly monolayer

Abstract

We introduce non-contact surface modification using trimethylchlorosilane (TMCS) for thin film transistor application. The surface is not contacted to the TMCS solution because it is vaporized at room temperature. The hydrophobic surface with contact angle of ~ 70° can be achieved by the transfer of TMCS using a PDMS mold.

1. Introduction

Surface modification has been studied for smart lithography to replace the conventional photo-lithography [1]. Especially, selective modification of the surface into hydrophobic or hydrophilic is necessary for the self organized coating or selective deposition for the fabrication of organic thin film transistor (OTFT) or organic light emitting diode (OLED) [2]. Octadecyltrichlorosilane (OTS) and hexadecanethiols (HDT) were widely used as self assembly monolayer (SAM) material [3] to change surface characteristics from hydrophilic to hydro-phobic. Usually surface modification was performed with bringing chemicals into contact with thin film surface. So it is not possible to avoid the contamination due to chemical contact in solution [4]. Here we introduced non-contact surface modification method using TMCS vapor for display application.

2. Experimental

We prepared UV ozone treated glass substrate. Glass was cleaned in IPA by ultra sonic for 10 minutes and rinsed in DI water. Then glass substrate was purged by pure nitrogen for drying substrate. The cleaned glass has very low contact angle with high surface energy [5]. Finally, we treated the 172 nm monochromatic UV-ozone for 5 minutes so that hydrophilic surface was achieved.

We put cleaned and hydrophilic treated bare glass in the vessel and then one drop of TMCS solution (99 %, Sigma Aldrich) was put onto the bottom of vessel as shown in Fig. 1. Then, the vessel was sealed in atmospheric condition just after the dropping the solution.
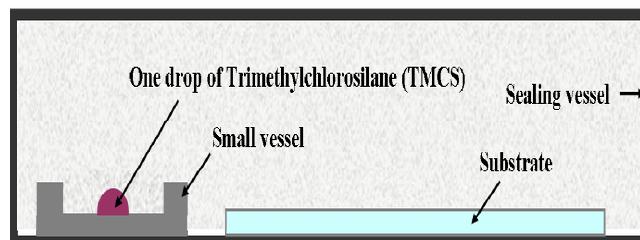

Fig. 1. Schematic diagram of TMCS vaporization treatment.

Figure 2 shows the chemical reaction of the TMCS vaporization treatment with the Si-OH treated surface [6]. We changed the treatment time from 0 to 300 sec and temperature of vessel from 25 to 70 ℃. After the treatment the contact angle of the sample was measured by the surface tension analyzer (surface-electro optics cooperation, Pheonix 600) using de-ionized water. We measured rms roughness of TMCS layer according to the vapor treatment time. Through the AFM analysis, we could observe the how the TMCS layer formed on the glass substrate as increasing the treatment time.
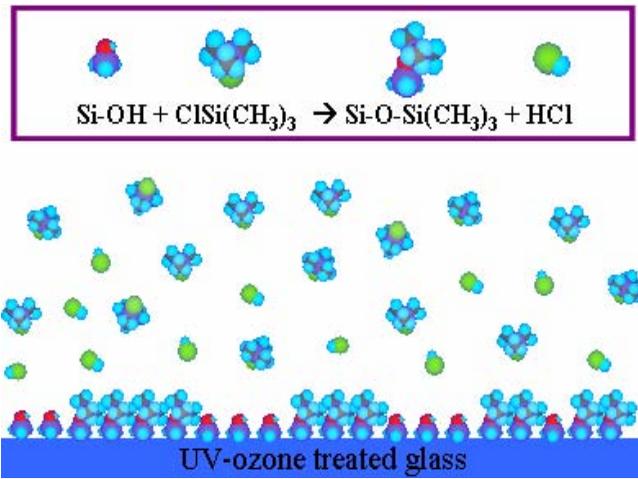
Fig. 2. Surface chemical reaction during TMCS vaporization treatment.

We treated the TMCS vapor onto the soft and hard polydimethylsiloxane (PDMS) mold for micro contact printing (μ-CP). Soft PDMS was cast and cured onto the flat surface at 80℃ for 3 hrs. Hard PDMS was made by 4 materials mixing (methylhydrosiloxane (HMS-301,Gelest), vinylmethylsiloxnedimethylsiloxane (VDT-731, Gelest), Platinumdivinyltetramethyldisiloxane (SIP6831.1, Gelest), and 2,4,6,8 tetramethyl-tetravinylcyclotetrasiloxane (Fluka)).

We coated the h-PDMS mixed material on flat surface and cured at 60 ℃ for 30 minutes. Then, s-PDMS was cast and cured onto cured h-PDMS at 80℃ for 3 hrs [7]. After the curing, we detached the mold from the flat surface. TMCS layer was also formed onto soft and hard PDMS using vapor treatment for 5 minutes. Finally we performed u-CP using TMCS treated soft and hard PDMS mold for transferring TMCS layer onto the glass substrate for 5 minutes. Then, contact angle of glass was measured to confirm the transferred TMCS layer.

3. Results and discussion

Figure 3 shows the surface energy change of TMCS treated glass substrate with increasing the TMCS treatment time at room temperature. Before the TMCS treatment we exposed UV-ozone onto the glass surface to make surface hydrophilic so that we can form TMCS layer on glass substrate [8]. Surface energy of the TMCS treated area decreased to below the 40 mN/m within 300 sec. With increasing the treatment time, the contact angle and surface energy started to saturate at 120 sec.
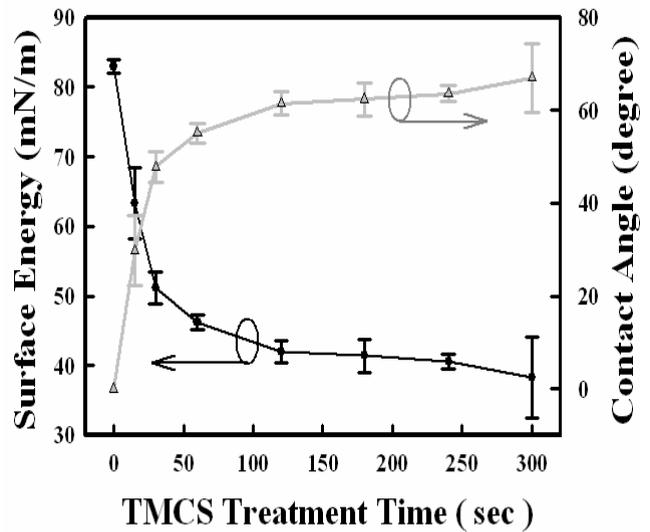

Fig. 3. Surface energy and contact angle variations of TMCS treated glass with increasing treatment time at room temperature.
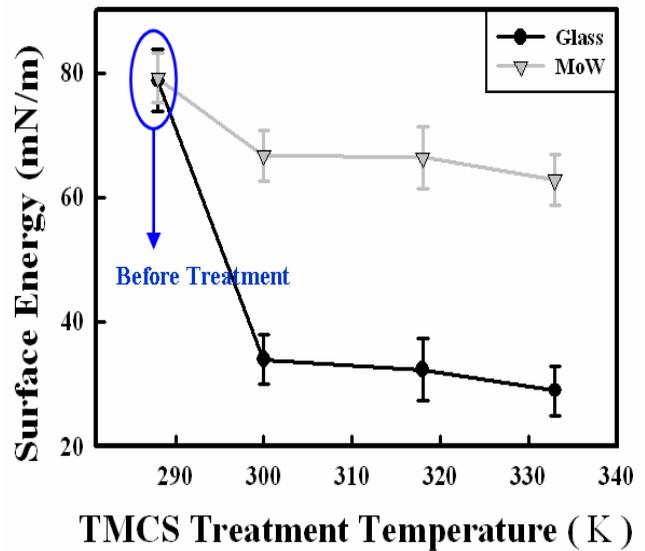

Fig. 4. Surface energy of TMCS treated glass and MoW films with increasing ambient temperature.

Figure 4 shows the surface energy change of the TMCS treated glass according to the ambient temperature. The surface energy of glass decreased a little with increasing the treatment temperature. We compare glass and MoW substrate. Surface energy change of MoW suface is smaller than that of glass.

TMCS treatment is more effective onto the glass substrate than MoW surface because the TMCS molecule react well with the Si-OH terminated surface as shown in Fig. 2.

TMCS treatment is more effective onto the silica surface or the Si-OH terminated organic surface than metal surface. Another disadvantage of this treatment is by-product of HCl vapor in TMCS treatment which attack metal surface during the treatment, especially in Ni.

Figure 5 shows the AFM images of the TMCS treated glass as a function of treatment time. The AFM image was obtained by scanning in area of 5×5 μm^2. The film seems to form from nuclei of TMCS on glass substrate as shown in this figure. The grain size ranges from 80 to 240 nm from this figure and its thickness is from 2 to 10 nm from the AFM images. Note that the length of a TMCS (Si(CH$_3$)$_3$Cl) layer is 5.6 Å and that of Si-O-Si(CH$_3$)$_3$) is 7 Å. Therefore, the TMCS layer composed of many layers.
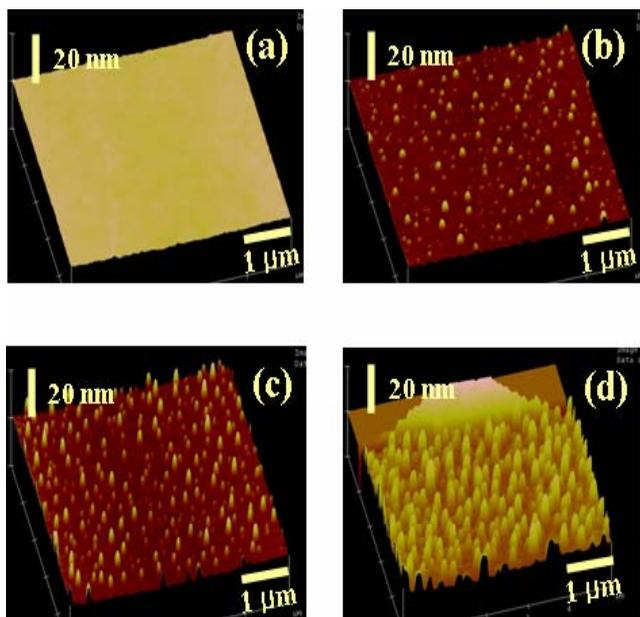

Fig. 5. AFM images of TMCS treated glass as a function of treatment time; bare glass (a), 15 sec (b), 60 sec (c) and 1800 sec (d).

Figure 6 shows that the rms roughness of TMCS layer increases as increasing the TMCS treatment time. RMS roughness was obtained from the scan area of 2×2 μm^2 from the image as shown in Fig. 5. RMS roughness increased to 9 Å within 15 sec and saturated at ~ 10 Å after 300 sec.
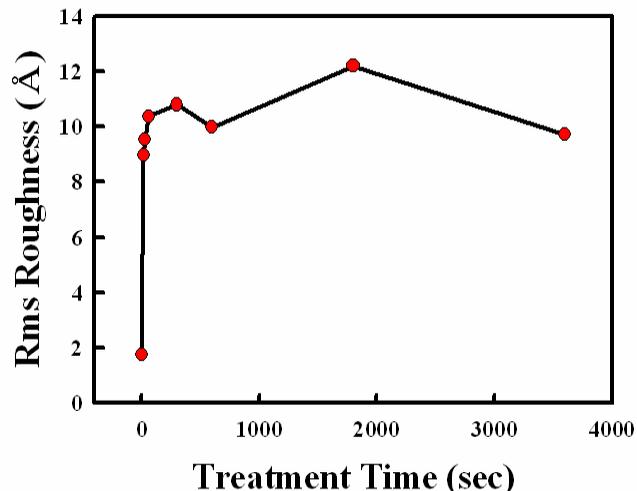

Fig. 6. RMS roughness of TMCS treated glass as a function of treatment time.

Figure 7 shows that contact angle of transferred TMCS layer on glass substrate by u-CP using h-PDMS and s-PDMS flat mold. Figure 6 (a) and (b) show that contact angle of glass decreased to zero by UV ozone treatment. The increase on glass indicates the presence of the transferred TMCS layer on glass surface just after u-CP process by s-PDMS and h-PDMS as shown in Fig. 7 (c) and (d). This also shows that TMCS layer can be formed in soft and hard PDMS mold by vapor treatment and can be transferred to the other substrate directly.
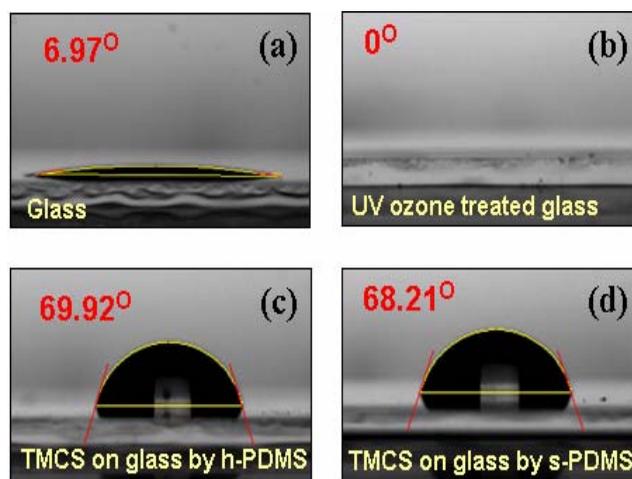

Fig. 7. Contact angle of bare glass (a), UV ozone treated glass (b), transferred TMCS onto UV ozone treated glass by h-PDMS mold (c) and by s-PDMS mold (d).

4. Conclusion

We introduce in this paper the TMCS vapor treatment for TMCS layer formation on glass and PDMS surface. Surface energy decreases with increasing the treatment time. Contact angle of TMCS treated glass increases a little with increasing the vessel temperature. It is found that TMCS vapor treatment is more effective onto the glass surface than MoW surface. The rms roughness of the TMCS layer increases up to 10 Å with increasing the treatment time. The TMCS layer can be transferred to other substrate by u-CP using s-PDMS or h-PDMS mold.

5. Acknowledgements

6. References

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