Selective Patterning of ITO on flexible PET Substrate by 1064nm picosecond Laser

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Abstract

Pulsed picosecond laser ablation of indium tin oxide (ITO) coated on flexible polyethylene terephthalate (PET) substrate has been investigated. Pulses with 355 nm, 532 nm and 1064 nm wavelengths are performed for comparison. Laser irradiation from the front side and the back side are analyzed. The single pulse ablation threshold is found at 0.56 J/cm² from the study of the spot sizes varied according to pulse fluence. The overlap rate in multi pulses ablation of ITO layer is discussed during the scribing of lines. Optical microscopy, SEM, surface stylus and EDX analysis reveal that the ITO layer can be completely removed with little damage of the PET substrate using optimized parameters.

Keywords: laser selective patterning; ITO patterning, flexible organic solar cell.

1. Introduction

Indium tin oxide (ITO) provides high electrical conductivity and optical transparency in visible wavelengths. It is widely used as transparent electrodes in industry, such as solar cells, liquid crystal displays, image sensors and so on. During the device fabrication, the ITO layer has to be locally selectively removed from the substrate to form special geometry for working as isolated electrodes. Except photolithography and etching in acid solutions approaches [1-3], laser direct writing for patterning of ITO conductive thin film on glass substrate has been studied for several decades and has been well established in industry [4]. Different laser sources have been applied to investigate the ablation behavior, such as excimer laser (248 nm) in [5], Nd:YLF laser (1047 nm, 523 nm and 262 nm) in [6-9], F2-laser (157 nm) [10] with pulse duration range from femtosecond, picoseconds to nanosecond [11,12]. However, laser patterning of ITO thin film on flexible polymer substrate have not obtained much research attention so far. Due to the fast development of flexible organic emitting diode displays (OLED) and flexible organic photovoltaics (OPV), the industry is looking for approaches to selectively remove ITO film from the polymer substrates. In this paper we try to address this issue by using picosecond laser ablation of ITO thin film on polyethylene terephthalate (PET) substrate.

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2. Experimental

ITO coated on PET foil is commercially available (Visiontek Systems Ltd.) with resistance of 50 Ω/sq. The thickness of the ITO film is 100 nm and the PET substrate is 175 µm thick. The optical properties of the sample at different wavelengths were measured by UV-Vis spectrophotometer (V-660, Jacob). The samples were subjected to laser pulses as purchased without any further treatment. Experimental set-up included a pulsed Nd:YAG laser with wavelengths of the fundamental 1064 nm, the second harmonic 532 nm and the third harmonic 355 nm. The pulse duration is 10 ps and the repetition rate was set to 200 kHz. The Gaussian beam diameter is 10 mm after the beam expander, an M2 quality parameter of 1.3. Galvanometric scanners (HurryScan14 for 1064 nm and 532 nm, HurryScan10 for 355 nm, Scanlab GmbH) equipped with F-theta lenses (LINOS) were used to move the beam relative to the sample. Pulse chain was assessed by controlling the open time of external electro-optic modulator (EOM), which capable of repetition rates from 0 up to 200 kHz. The whole system diagram is shown in figure 1. The depth and width of ablated spots and lines were measured from stylus profile obtained by white-light interference microscope (TMS-1200, Polytec. GmbH), stylus profilometer (XP-2, Ambios Technology) and scanning electron microscope (SEM). The ablation morphology was also analyzed with the SEM pictures accompanied by energy dispersive X-ray spectroscopy (EDX).

![Figure 1. The schematic diagram of laser ablation system](image)

3. Results and Discussion

A set of experiments were conducted to investigate the picosecond laser ablation of ITO on PET substrate. Ablation effects with different wavelengths, laser irradiation directions, laser fluences and number of pulses were presented and discussed.

3.1 Different wavelengths ablation experiment

Pulse wavelengths could affect the ablation process due to the absorption behavior of the ITO material and PET substrate when exposed to the laser pulse. The optical spectral transmittance and reflectance measurements were made by UV-VIS spectrophotometer. The absorption coefficients were derived by combining the thickness of ITO layer (100 nm) and PET substrate (175 µm) as well as the virgin PET substrate without coating. Figure 2 shows the calculated absorption coefficients at different wavelengths. The derived curve reveals that the absorption coefficient of ITO material has nearly 103 times higher than PET material in the detected spectral range, especially at IR and UV regime. This indicates the possibility to selectively remove of ITO layer without damaging the PET substrate. Actually from the experiments investigation, the three wavelengths pulse were able to selectively remove of ITO layer, as shown in figure 3. The ITO material was punched out from the PET substrate by single pulse. However, the 1064 nm pulses ablation demonstrates much smoother and clearer rim than 532 nm and 355 nm pulses at the edge of ablation spots. The 532 nm and 355 nm pulses induced kind of delamination effect no matter what pulse energy...
above the ablation thresholds was applied. The detached ITO thin film at the edge was curled from the central part of the ablated spots due to the stress gradient generated by Gaussian laser beam, which also induced some cracks to the non removed area. This makes it difficult to obtain clean edge of the ablation area for industrial application without further beam shaping. For this reason in this paper we focus on investigation of 1064 nm wavelength pulses.

Figure 2. Absorption coefficients of ITO and PET material.

Figure 3. Ablation spots induced by different wavelength pulses. (a). 355 nm. (b). 532 nm. (c). 1064 nm.

3.2 Single-pulse experiment

The single pulse ablation spot was obtained by setting the laser pulse repetition at 200 kHz and laser scanning speed up to 5 m/s. First we investigated the different laser irradiation direction, named as front-side and back-side ablation effect on the ablation spot illustrated in figure 4(a). There was some literature discussing about the difference for patterning of thin film in solar cells application [13, 14]. Here much difference was observed between front-side and back-side ablation, as shown in figure 4(b) and figure 4(c) respectively. The font-side ablation induced lots of curled strips at the edge of ablated spot, leading to an unclear ablation spot. Pieces of fragments were observed in this case. While the back-side ablation demonstrated cleaner and sharper spots with little delaminated strips at the rim. Based on the results in the following analysis, back-side irradiation was performed.

Figure 4. (a). Front-side and back-side laser irradiation direction for ablation. (b). Front-side ablation spot. (c). Back-side ablation spot.

Removal of a material by laser beam with Gaussian radial energy greater than the ablation threshold energy $E_{th}$. 

the relationship between the spot size and the applied laser energy can be derived by solving the Gaussian beam equation, which yields,

\[ D^2 = 2\omega_0^2 \ln \left( \frac{E}{E_{th}} \right) \]

where \( D^2 \) is the squared ablation spot diameter, \( \omega_0 \) is the effective laser focus spot diameter, \( E \) is the pulse energy and \( E_{th} \) is the ablation threshold pulse energy. This formula can be used to derive the focus size and the ablation threshold [15]. Figure 5(a) shows the single-pulse ablation spots squared-diameters produced with different pulse energies followed a linear fitting operation, plotted on a logarithmic scale. From the slope of the linear fitting data, the effective laser focus spot diameters can be calculated as \( \sqrt{440/2} = 14.8 \mu m \). The ablation fluence was derived using this effective focus diameter. The ablation energy threshold can be obtained by extrapolating the fitting line to the intercept of energy axis, where the ablation spot diameter was regarded to be zero. By using

\[ F_{th} = 2E_{th}/(\pi\omega_0^2) \]

the ITO ablation threshold was calculated as 0.56 J/cm².

At fluences lower than the ablation threshold, where the ITO layer was not ablated through the whole layer thickness but visible damage of the ITO surface was observed, a damage threshold fluence \( F_d \) could be defined, experimentally found at around 0.5 J/cm². For completely removal of the ITO layer, the pulse fluence has to be a little higher than the calculated threshold 0.72 J/cm². From the experiment we found that when the pulse fluence was above 0.89 J/cm², the layer could be totally removed. On the other hand, as the pulse fluence increased, the underlying PET suffered higher heat affects and could be damaged when the fluence exceed a certain value, defined as PET substrate damage threshold \( F_{d,PET} \). In figure 5(b) the ablation depth varies with different pulse fluences was plotted. From the figure we can see at some the pulse fluences the ablation depth exceeds the ITO layer thickness of 100 nm, which means the PET substrate has been damaged. With a linear fitting in the PET damaged range, similar to ablation threshold of ITO layer, the PET damage threshold can be derived, calculated as 1.81 J/cm². Therefore the suitable processing window of the pulse fluence for removal of ITO layer without damaging the substrate was between 0.89 J/cm² and 1.81 J/cm².

3.3 Multi-pulse overlapped experiment

Contrary to single-pulse ablation, selective scribing of lines or patterning of an area is the result of multi pulses ablation process. Lines are used at most for structuring ITO layers. A trench on ITO layer will electrically isolate the
two sides from each other. Therefore, all ITO should be removed. By setting the laser fluence slightly above the ablation threshold, superior quality ablation spots could be obtained. Moreover, in addition to the pulse fluence, the separating distance between the adjacent pulses, which is usually expressed in term of overlap rate, is another one of the most important factors in multi pulses ablation. The definition of overlap rate is illustrated in figure 6 with its mathematical equation.

\[
\text{Overlap rate} = \frac{D - d}{D} \times 100\%, \quad 0 < d \leq D
\]

Figure 6. The illustration and the mathematical equation of the definition for overlap rate.

Where D is the spot diameter induced by single pulse, d is the distance between adjacent spots. When \(d > D\), the overlap rate is regarded as 0%. The extreme case \(d = 0\), the overlap rate is 100%, when the multi pulses of the same energy are incident on the same surface location. Figure 7 shows the ablation spots induced by 4 pulses, 7 pulses and 10 pulses. As the pulse number increased, the spots size increased. Also we can see the heat effect area around the spots diffused further, which affected the edge of ablation area and made the rim not as smooth as less pulses ablation. The variation can be explained by the effects of incubation, which is determined by the nature of the material.

Figure 7. Heat affect zone induced by different number of pulses irradiation. (a). 4 pulses. (b). 7 pulses. (c). 10 pulses.

The existed incubation behavior matters when patterning lines or areas, which are the results of partly overlapped single pulse ablation. Examples of patterning lines with different overlap rate are shown in figure 8, taken from microscopy. For lower overlap rates, the edges of the ablation trench were much clearer and the substrate PET suffered less heat affect from the ablation of upper ITO material, but meanwhile it had higher risk of electrical interlinked path through the trench. As the overlap rate increased, the ablation trench width and depth increased, which can be easily seen in figure 9. Meanwhile, the greater overlap rate, more and more small sharp sawtooth emerged along the edge. Visible damage of the PET substrate was appeared as the overlap rates exceed 50%.
Summarizing, the challenge always comes from how to decrease the shoulder height and make them smooth at the rim of the ablation area. As discussed above, back-side irradiation, fluence slightly above ablation threshold and relatively lower overlap rate could lead to superior quality of patterning results. By synchronously optimizing these parameters, clear selective patterning of ITO lay could be achieved by 1064nm pulse illustrated in figure 10. The laser fluence applied here was 0.85 J/cm² and the overlap rate was 15%. For better observation, the sample has been tilted for pictures and the cross section profile was measured by stylus profile meter. From the SEM picture we can see that the edges of the patterned trenches are sharp and clean. No apparent damage of PET substrate was observed. The profile of the scribed trench revealed that the etching depth was approximately the same as the ITO layer thickness of 100 nm. The shoulder height at the edge was measured below 20 nm.
Figure 10. (a). Line patterns by 1064nm pulses with overlap rate 15%. (b). Cross section profile of the patterned line measured by stylus profile meter.

Figure 11 shows another example of selective area removal of ITO layer conducted by 1064nm laser pulses. The overlapping rate was set to 30% and the laser fluence used was 0.85J/cm². Figure 11(b) shows the cross section profile. The 100 nm thick ITO layer was totally removed with only small damage to the PET substrate.

EDX analysis of the relative content of indium was carried out along the solid line shown in figure 12(a), located in the ITO removal area. For reference, EDX characterization of native ITO coated PET was also detected shown as dashed line. The results are plotted in Figure 12 (b) respectively. The contrast in the contents of indium demonstrates the complete removal of the ITO layer and verifies the selective patterning ability of 1064 nm picosecond laser pulses.

Figure 12. EDX measurements of the relative content of indium in the ablated area (solid line) and the virgin ITO surface (dash line).
4. Conclusion

Fundamental and systematical investigations have been accomplished to study the significant ablation behavior of picoseconds laser irradiation on ITO thin film on PET substrate. It has been shown that the fundamental 1064 nm wavelength pulses with back-side irradiation demonstrate better performance compared to second harmonic 532 nm and third harmonic 355 nm wavelengths pulses. The single pulse ablation threshold of 0.56 J/cm² is proposed derived from the spots diameter varies with pulse fluences. Experimental studies reveal overlap rate less than 50% demonstrate lower heat accumulation effect. Therefore less damage to the PET substrate and smoother ablation rim. Superior quality of the patterning lines and areas were obtained by synchronously optimizing the laser pulse fluence and pulses overlap rate with back-side irradiation strategy.

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