Angle resolve x-ray photoelectron spectroscopy analysis of La$_2$O$_3$ thin film of mixed carbon-glass and carbon-silicon substrate for micro-flexographic printing process

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Abstract. Adhesive property could be described as an interchangeably with some ink and substrate which was applied to one surface of two separate items that bonded together. Lanthanum oxide (La$_2$O$_3$) had been used as a rare earth metal candidate as printing ink. This metal deposit was printed on carbon-silicon substrate and carbon-glass substrate using Magnetron Sputtering technique. The choose of Lanthanum Oxide as a target is due to its wide application in producing micro-electronic devices such as thin film battery, electronic circuit and printed circuit board. The La$_2$O$_3$ was deposited on the surface of carbon-silicon and carbon-glass substrate were then analyzed using Angle Resolve X-Ray Photoelectron Spectroscopy (ARXPS). The position for each synthetic component in the narrow scan of Lanthanum (La) 3d and O 1s were referred to the electron binding energy (eV). This research was focused on the narrow scan regions which were O 1s and La 3d. Further discussion of the spectrum evaluation was discussed in detail. Here, it was proposed that from the adhesive and surface chemical properties of La was suitable as an alternative medium for micro-flexographic printing technique in printing multiple fine solid lines image at micro to nano scale feature. Micro-flexographic printing was developed in patterning technique from micron to nano scale range to be used for graphic, electronic and bio-medical device on variable substrates. Hence, this paper will describe the capability of this particular metal as rare earth metal in a practice of micro-flexographic printing process.

1. Introduction
Printing was a process reproducing an images using master form or printing plate. By combining both printing techniques which was micro-contact and flexographic also known as micro-flexographic printing had its own advantages and disadvantages, a new era of printing technology could be explored in producing micro to nano scale printing image[1]. The printed image was then analysis using Angle Resolve X-Ray Photoelectron Spectroscopy (ARXPS) to find the adhesive and chemical property between ink and substrate [2].

The attraction strength between two adhesive or printed material was determined by the surface energy of the material. Adhesion was the molecular force of attraction between unlike materials for example lanthanum oxide metal and mixed carbon-glass or carbon-silicon substrate. The higher surface
energy, the molecular attraction will be greater. Particles size of La$_2$O$_3$ bulk were in the region of 1 µm which had been examined using Scanning Electron Microscopy (SEM) [3].

The chemical bonding between La metal deposited and substrate surface was due to a chemisorption and physisorption process. The adhesion property of La$_2$O$_3$ on Si substrate was successful when O 1s binding energy can be seen from La$_2$O$_3$ and SiO$_2$ components. There were four components that contributed to O 1s photoelectron which were La$_2$O$_3$, SiO$_2$, O bulk and water vapour [4].

The addition of pure La could give high denitriding rate compared with the experiment without La addition. La element can reduce the N contents in nitriding layers through the surface oxidation and attraction of La atoms [5]. The work and result had been analyzed and investigated by using X-ray diffraction (XRD), scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS) and micro hardness tester.

Other than lanthanum material, graphene was the other example of rare earth metals that could be used as printing ink for micro-flexography printing. Graphene ink was a step to move forward in order to achieve high speed printing in electronic with simple, rapid, low cost method, less waste and roll-to-roll capability. This type of ink was practically used in electronic printing industries that aimed on printing multiple micro to nano solid lines [6].

Previous research had shown that printing components played an important roles in producing micro to nano scale printing image with a good adhesive property. The example of printing components were ink, printing plate, substrate, anilox and others. The ink properties could be ink chemistry, viscosity, rheological behavior, solvent evaporation rate and drying [7].

Previous research in fine solid line printing, the researcher [8] managed to print out 50µm line width and 50µm line gap by using carbon graphic inks as printing inks. The author used web press industrial machine as a printing method. This technique used photopolymer as a mould to transfer the ink from plate roller to substrate. While, in micro-contact printing (µCP), Perl showed that µCP could produce fine solid line below 1µm [9] which was smaller than flexography printing technique. The combination of both printing techniques hope will produce better image in micro to nano scale features.

Lanthanum was a suitable material to use in printing process because it will oxidize when exposed to air. Lanthanum material had been used as La$_{0.15}$Sr$_{0.85}$FeO$_3$ (LSFO) film in screen printing process in powders element synthesize by sol-gel. The lanthanum film had good sintering properties and fair compatibility with alumina ceramic substrates. The value of electrical conductivity was also high [10].

Lanthanum oxide characteristics was the most important issue that must be understood either it was suitable to be used as a printing ink for combination of flexography printing and µCP which known as micro-flexographic [11]. This study was investigated on the possibility of using lanthanum oxide ink in micro-flexographic to achieve the printing fine solid lines and good surface adhesion on mixed carbon-silicon and carbon-glass substrate.

2. Research Methodology

The micro-flexographic printing process was began from the preparation of printing plate. A pattern of fine solid line image was produced on printing plate [12] which was attached at plate cylinder. Micro-flexographic printing process was almost same as flexographic printing process [13]. Ink was transferred to the printing plate by using an engraved cylinder known as an anilox roll as shown in figure 1. Here, the thin film analysis had been performed into two categories which were deposition process of lanthanum using magnetron sputtering techniques and surface characterization using ARXPS. The take-off angle had been performed within 0° to 45° in subsequence order. At 0° take off-angle, analysis was reflected to the surface analysis for the bulk of the substrate while at grazing take-off angle, 45°, the others surface composition was determined for the uppermost oxide layer of mixed carbon-silicon and carbon-glass substrate.

X-ray Photoelectron Spectroscopy (XPS) was an advanced surface analytical techniques that used to characterize the elemental composition of the lanthanum oxide printing ink. The method was favourable for several nanometer thickness oxide or deposition [14]. XPS spectrum were obtained on an Omicron Nanotechnology spectrometer equipped X-ray source powered at 300W (15kVe20 mA) and operated
under ultra-high vacuum (UHV) condition at $10^{-11}$ Torr. The kinetic energies of the photoelectrons were measured using a hemispherical electron analyser working in the fixed analyser transmission (FAT) pass energy mode, of 180 eV and 20 eV for wide and narrow scanning respectively.

![Figure 1. Schematic description of the micro-flexographic printing process](image)

Spectrum analysis of variable angles were deconvoluted using Casa XPS software. The synthetic spectrum for the photoelectron peaks and its background signal was optimized using a specific model. Here, the appropriate background model used was Shirley method, while the synthetic photoelectron signal assigned using mixed of Gaussian-Lorentzian method with ratio 70% and 30% respectively. In this work, the data deconvolution was performed for element of interest on the substrate by referring to the narrow scan. There region of interest which were Lanthanum, La 3d, and oxygen, O1s.

Generally, lanthanum oxide had chemical properties that meet the requirements for applications in various electronic fields. The base material for the samples used in this study was commercially available lanthanum oxide target. La$_2$O$_3$ was known to spontaneously react with humidity in air to form lanthanum hydroxide La(OH)$_3$ [15]. Surface chemistry of lanthanum oxide could be produced, but the high reactivity of this compound will cause a rapid roughening of the surface due to the formation of hydroxides or carbonates.

RF magnetron sputtering was a suitable technique to print rare earth metal or metal oxide liked lanthanum oxide on variable substrates [16]. Recently, the fabrication of lanthanum oxide (La$_2$O$_3$) on substrate had been investigated intensively in the global scale [15]. Since there were few researchers correlated the properties of depositing La$_2$O$_3$ on carbon-silicon and carbon-glass substrate, the understanding to produce high-quality La$_2$O$_3$ printed using magnetron sputtering was poor.

3. Result and Analysis
The position for each synthetic component in the narrow scan of La 3d and O 1s were referred to the electron binding energy (eV). The spectrum analysis was deconvoluted by Casa XPS software. There were 4 series of take-off angle involved in these experiments as mentioned in the previous methodology section.

Firstly, the experiment analysis for the bulk of the carbon-silicon substrate was carried out at the angle of 0°. The deconvolution of O 1s photoelectron spectrum for La$_2$O$_3$ indicated that the oxygen species were comprises different peaks at 528.9, 530.3, 531.7 and 533.2 eV associated with SiO$_2$, bulk, La$_2$O$_3$ and OH$^-$ as illustrated in figure 2(a). Then, the experiment analysis was continued for the bulk of the carbon-glass substrate which also carried out at the angle of 0°. The deconvolution of O 1s photoelectron spectrum for La$_2$O$_3$ indicated that the oxygen species were comprises different peaks at 528.9, 530.2, 531.5 and 532.7 eV associated with SiO$_2$, bulk, La$_2$O$_3$ and OH$^-$ as illustrated in figure 2(b).

At take-off angle 15°, the deconvolution of O 1s photoelectron spectrum for La$_2$O$_3$ on carbon-silicon substrate indicated that the oxygen species were comprises different peaks at 528.5, 530.2, 532.5 and 534.0 eV associated with SiO$_2$, bulk, La$_2$O$_3$ and OH$^-$ as illustrated in figure 3(a). While, the
deconvolution of O 1s photoelectron spectrum on carbon-glass substrate indicated that the oxygen species were comprises different peaks at 528.0, 530.0, 531.2 and 532.6eV as illustrated in figure 3(b).

![Figure 2. XPS spectrum deconvolution for O 1s (a) on carbon-silicon substrate and (b) on carbon-glass substrate in 0° take-off angle](image)

![Figure 3. XPS spectrum deconvolution for O 1s (a) on carbon-silicon substrate and (b) on carbon-glass substrate in 15° take-off angle](image)

Then, experiment analysis of mixed carbon-silicon substrate was carried out at the angle 30°. The deconvolution of O 1s photoelectron spectrum for La$_2$O$_3$ indicated that the oxygen species were comprises different peaks at 527.7, 529.1, 533.6 and 535.1eV as illustrated in figure 4(a). The deconvolution of O 1s photoelectron spectrum for La$_2$O$_3$ on carbon-glass substrate indicated that the oxygen species were comprises different peaks at 528.0, 530.2, 531.5 and 533.0eV as illustrated in figure 4(b) which associated with SiO$_2$, bulk, La$_2$O$_3$ and OH respectively.

The last analysis for the bulk of the mixed carbon-silicon substrate was carried out at the angle of 45°. The deconvolution of O 1s photoelectron spectrum for La$_2$O$_3$ indicated that the oxygen species were comprises different peaks at 527.8, 529.2, 530.3 and 531.5eV as illustrated in figure 5(a). The deconvolution of O 1s photoelectron spectrum for La$_2$O$_3$ on carbon-glass substrate indicated that the oxygen species were comprises different peaks at 529.1, 530.8, 532.2 and 533.9eV as illustrated in figure 5(b) which associated with SiO$_2$, bulk, La$_2$O$_3$ and OH respectively.

From both carbon-silicon and carbon-glass substrate overall result, the high insensitive of photoelectron signal from both oxides at 45° take-off angle had become a clear evidence to support this finding. It means that most of the lanthanum oxide deposited was residual at the upper most layer of the substrate which at the bulk of the substrate. The information of oxygen species, O$^2-$ component from O 1s narrow scan indicated there were 4 species of oxygen associated with the O 1s signal which were contributed by SiO$_2$, bulk oxide, La$_2$O$_3$ and hydroxide components. Here, two surface chemical process involved in oxide formation bonding which was chemisorption and physisorption process. It was cleared that the metal oxide bonding La$_2$O$_3$ was formed from the chemisorption process whiles the hydroxide
component from physisorp process. This was evidenced that the deposited of Lanthanum metal with carbon-silicon substrate and carbon-glass substrate were bonded together with the substrate surface.

Figure 4. XPS spectrum deconvolution for O 1s (a) on carbon-silicon substrate and (b) on carbon-glass substrate in 30° take-off angle

Figure 5. XPS spectrum deconvolution for O 1s (a) on carbon-silicon substrate and (b) on carbon-glass substrate in 45° take-off angle

Therefore, it could be concluded that the surface adhesion of the Lanthanum metal deposited was better on carbon-glass substrate compared to carbon-silicon substrate. At take-off angle 45° of O 1s photoelectron spectrum, binding energy position at La₂O₃ on carbon-glass substrate (532.2) was higher than carbon-silicon substrate (530.3) as shown in table 1. The formation of this bonding was respected to a good adhesion between metal deposited and substrate due to the anion and cation interaction under a thermodynamic influenced. Hence most of the signal at this 45° take-off angle was mainly contributed by photoelectron from La₂O₃.

Table 1. A comparison at O 1s component between carbon-silicon and carbon-glass substrate.

| Substrate       | Binding Energies Position (eV) At Take-Off Angle 45° |
|-----------------|------------------------------------------------------|
|                 | O (SiO₂)    | O (bulk)   | O (La₂O₃) | O (OH⁻) |
| Carbon-silicon  | 527.8       | 529.2      | 530.3      | 531.5   |
| Carbon-glass    | 529.1       | 530.8      | 532.2      | 533.9   |

4. Conclusion
Surface adhesion study of La₂O₃ deposits on carbon-glass substrate compared to carbon-silicon substrate was successfully done. There were two types of oxide species on the substrates which were La₂O₃ and SiO₂. The oxide components that contribute to O 1s photoelectron were SiO₂, bulk, La₂O₃ and OH⁻ (water vapour). The chemical bonding formation between the La metal deposited and the surface was
due to a chemisorption and physisorption process. A successful observation of La$_2$O$_3$ adhesion property on carbon-glass substrate was better than carbon-silicon substrates which clearly seen from the O 1s binding energy from La$_2$O$_3$ component. For conclusion, the micro-flexographic was good candidate for printing electronic with rare earth metal inks property, substrates and process parameters were main role to success the implementation.

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