A Study Of Printed La_2O_3 On Carbon-Glass Substrate For Micro-Flexographic Printing Process Using Angle Resolve X-Ray Photoelectron Spectroscopy (ARXPS) Analysis

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ABSTRACT

Micro-flexographic printing process involved in patterning technique from micron to nano scale range to be used for graphic, electronic and bio-medical device on variable substrates. Adhesive property of printing process could be described as an interchangeably with some ink or medium and substrate which was applied to one surface of two separate items that bonded together. Lanthanum oxide (La_2O_3) had been used as a rare earth metal candidate as printing ink medium. This metal deposit was printed on carbon-glass substrate. The choose of Lanthanum Oxide as a target is due to its wide application in producing electronic devices such as thin film battery and printed circuit board. The La_2O_3 deposited on the surface of carbon-glass substrate was 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 are referred to the electron binding energy (eV). This research was focused on 3 narrow scan regions which are C 1s, O 1s and La 3d. Further discussion of the spectrum evaluation was discussed in detail. Here, it was proposed that from the adhesive 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. Hence, this paper will describe the capability of this particular metal as rare earth metal in a practice of micro-flexographic printing process.

ABSTRAK

Proses pencetakan mikrofleksografik terlibat dalam teknik corak dari mikron hingga skala skala nano untuk digunakan untuk peranti grafik, elektronik dan bio-perubatan pada substrat berubah. Properties pelekat proses percetakan boleh digambarkan sebagai bergantian dengan beberapa dakwat atau medium dan substrat yang digunakan untuk satu permukaan dua barang berasingan yang terikat bersama. Lanthanum oxide (La_2O_3) telah digunakan sebagai calon logam nadir bumi sebagai media dakwat percetakan. Deposit logam ini dicetak pada substrat kaca-karbon. Memilih Lanthanum Oxide sebagai sasaran adalah disebabkan oleh aplikasi yang luas dalam menghasilkan alat elektronik seperti bateri filem tipis dan papan litar bercetak. La_2O_3 yang didepositkan pada permukaan substrat kaca-karbon kemudiannya dianalisis menggunakan Angle Resolve X-Ray Spectroscopy Photoelectron (ARXPS). Kedudukan bagi setiap komponen sintetik dalam imbasan sempit Lanthanum (La) 3d dan O 1s dirujuk kepada tenaga ikatan elektron (eV). Kajian ini difokuskan pada 3 kawasan imbasan sempit iaitu C 1s, O 1s dan La 3d. Perbincangan lanjut tentang penilaian spektrum dibincangkan secara terperinci. Di *sini, dicadangkan bahawa dari sifat pelekat La telah sesuai sebagai medium alternatif bagi teknik percetakan mikrofleksi dalam mencetak pelbagai imej garis padat halus pada ciri skala mikro ke nano. Oleh itu, makalah ini akan menggambarkan keupayaan logam tertentu ini sebagai logam nadir bumi dalam amalan proses percetakan mikrofleksi.*

Keywords: Micro-flexographic printing, Angle Resolve X-Ray Spectroscopy Photoelectron, Lanthanum Oxide

INTRODUCTION

From current research updated, the researchers had shown that printing components such as ink, printing plate, substrate, anilox and others, play important roles in producing the micro to nano scale printing image. Ink and substrate properties play the main role to achieve the best quality of printing. Examples of ink properties are ink chemistry, viscosity, rheological behaviour, solvent evaporation rate, drying and others [1].

The 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[2]. 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 [3].

Adhesion property was the molecular force of attraction between unliked materials for example lanthanum oxide metal and carbon-glass substrate. The attraction strenght between two printed material was determined by the surface energy of the material. The higher surface energy, the molecular attraction will be greater. Particles size of La_2O_3 bulk were in the region of 1 µm which had been examined using Scanning Electron Microscopy (SEM) [4]. These nanoparticles were almost spherical in shape and uniform in size of about 100 nm. There were four components that contributed to O 1s photoelectron which were La_2O_3, SiO_2, O bulk and water vapour [5].

The experiment with addition of pure La could give high denitriding rate compared with the analysis without La addition [6]. 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. This type of ink was practically used in electronic printing industries that aimed on printing multiple micro to nano solid lines [7].

Previous research on 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 as shown in figure 1. 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. This research used heavy-weight dendritic thioethers as inks and octadecanethiol as backfilling agent.

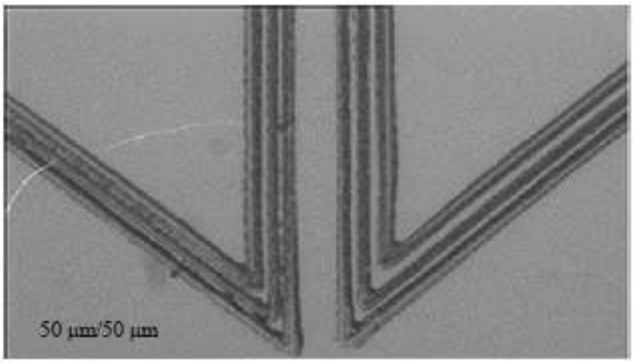


Figure 1. Fine line printing using photopolymer printing plate.

Lanthanum was a rare earth metal that suitable to use in printing process because it will oxidize when exposed to air. 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 micro-flexographic printing [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 property on carbon-glass substrate.

RESEARCH METHODOLOGY

The roller printing concept was a good method in mass production printing. The first step in micro-flexographic printing process was the preparation of printing plate. A pattern of fine solid line image was produced on printing plate [12] which was attached at plate cylinder. Ink was transferred to the printing plate by using an engraved cylinder [13] known as an anilox roll as shown in figure 2. The ink characteristic was studied by referring to its morphology, size and depth of engrave cells. 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 angle resolve XPS (ARXPS). The take-off angle had been performed within 0° to 15°. At 0° take off-angle analysis was reflected to the surface analysis for the bulk of the substrate while at grazing take-off angle, 15°, the others surface composition was determined for the uppermost oxide layer of carbon-glass substrate.

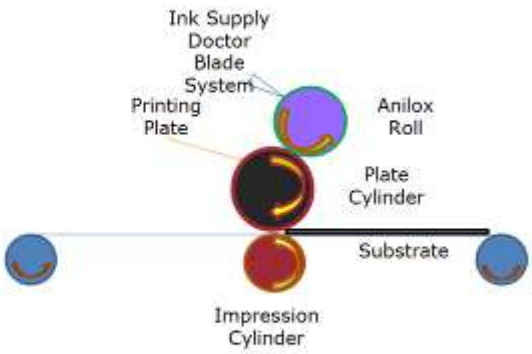


Figure 2. Schematic description of the micro-flexographic printing process.

X-ray Photoelectron Spectroscopy (XPS) was used to characterize the elemental composition of the lanthanum oxide printing ink [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.

The spectrum of variable angles were analysed using Casa XPS software. This software was capable to manipulate the spectrum iteration for photoelectron and background signal [15]. 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. The ratio for both Gaussian and Lorentzian had been assigned using 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.

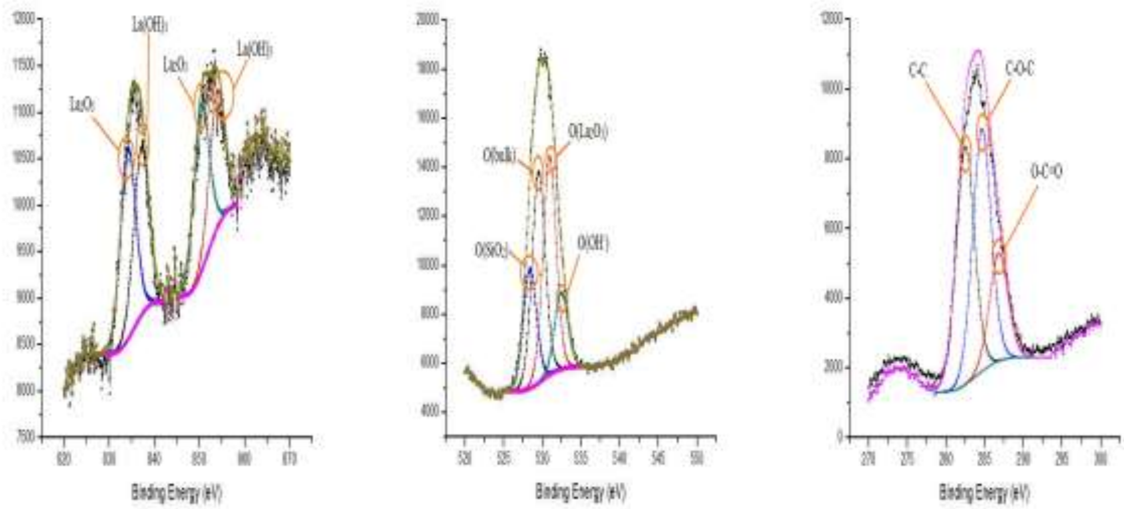
Lanthanum oxide had chemical properties that suitable for applications in various fields such as thin film battery, printed circuit board and others. The base material for the samples used in this study was commercially available lanthanum oxide target. La_2O_3 was known to spontaneously react with humidity in air to form lanthanum hydroxide $La(OH)_3$ [16]. The samples were characterised in form as it is difficult to produce compact bulk samples of these compounds with surfaces that are smooth on an atomic scale. 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 technique to print metal oxide on variable substrates. Basically, metal oxide thin film was achieved using the combination of inert gas and reactive gas during the sputtering deposition [17]. The fabrication of lanthanum oxide (La_2O_3) on substrate has been investigated intensively in the global scale [16]. Magnetron sputtering was one of the simplest and effective techniques to growth La_2O_3 printed on carbon-glass substrate. Since there were not many researchers correlated the properties of depositing La_2O_3 on carbon-glass substrate, the understanding to produce high-quality La_2O_3 printed using magnetron sputtering was poor. Therefore, in the present study, we focussed on investigating the properties of RF magnetron sputtering using La target. The sputtering was produced in Ar gas and $Ar/0_2$ gases mixture ambient.

RESULTS AND ANALYSIS

The position for each synthetic component in the narrow scan of La 3d, C 1s and O 1s were referred to the electron binding energy (eV). The spectrum analysis was deconvoluted by Casa XPS software [18]. There were 2 series of take-off angle involved in these experiments as mentioned in the previous methodology section.

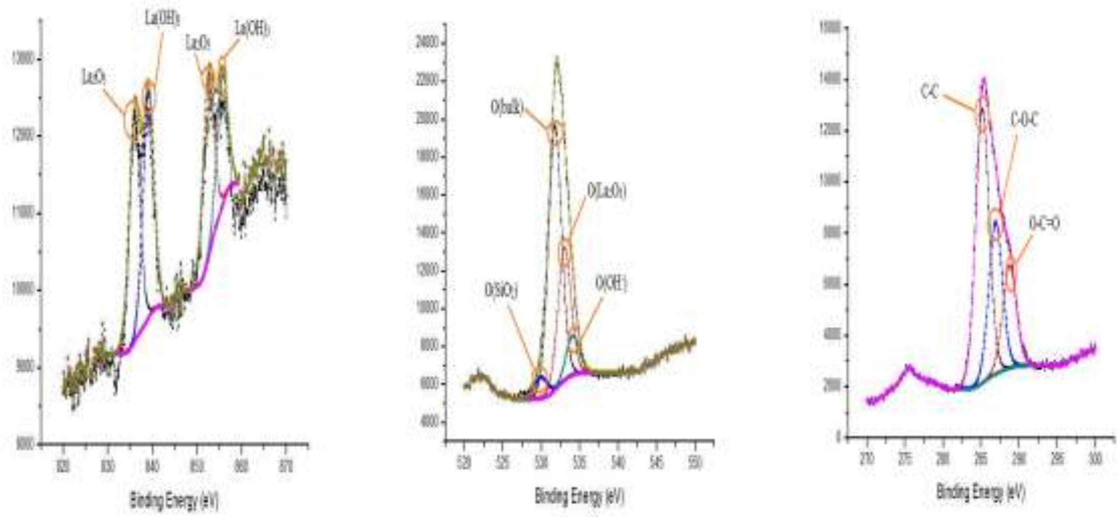
The first experiment analysis for the bulk of the carbon-glass substrate was carried out at the angle of 0°. The deconvolution of La 3d photoelectron spectrum for La_2O_3 were contributed by La_2O_3 and $La(OH)_3$ species with binding energy position of 834.2, 837.1, 850.4 and 854.0 eV respectively as shown in figure 3(a). Then, the deconvolution of O 1s photoelectron spectrum for La_2O_3 indicated that the oxygen species were comprises different peaks at 528.4, 529.5, 530.9 and 532.4 eV associated with SiO_2, bulk, La_2O_3 and OH^- as illustrated in figure 3(b). The deconvolution of C 1s photoelectron spectrum for C were contributed by C-C (282.5), C-O-C (284.6) and O-C=O (286.8) components as shown in figure 3(c).



(a) (b) (c)

Figure 3. XPS spectrum deconvolution for (a) La 3d, (b) O 1s and (c) C 1s for La_2O_3 on carbon-glass in 0° take-off angle.

At take-off angle 15°, the deconvolution of La 3d photoelectron spectrum for La_2O_3 were contributed by La_2O_3 and $La(OH)_3$ species with binding energy position of 835.9, 839.1, 852.5 and 855.6 eV respectively as shown in figure 4(a). The deconvolution of O 1s photoelectron spectrum for La_2O_3 indicated that the oxygen species were comprises different peaks at 529.9, 531.8, 533.0 and 534.1 eV as illustrated in figure 4(b). The deconvolution of C 1s photoelectron spectrum for C were contributed by C-C (285.1), C-O-C (286.9) and O-C=O (288.7) components as shown in figure 4(c).



(a) (b) (c)

Figure 4. XPS spectrum deconvolution for (a) La 3d, (b) O 1s and (c) C 1s for La_2O_3 on carbon-glass in 15° take-off angle.

From carbon-glass substrate overall result, it indicated that the La 3d narrow scan revealed the oxide species of this particular metal deposited was mainly contributed by La_2O_3 and $La(OH)_3$ species. It also noticed that the intensity for both oxide species increased significantly as the take-off angle varies from 0° to 15° take-off angle. This indicated that most of both oxides were sticking at the upper most surface.

The high insensitive of photoelectron signal from both oxides at 15° 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, and not 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_2O_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_2O_3 was formed from the chemisorption process while the hydroxide component from physisorp process. This was evidenced that the deposited of Lanthanum metal with carbon-glass substrate was bind together with the substrate surface.

Therefore, it could be concluded that the surface adhesion of the Lanthanum metal deposited was better at take-off angle 15° compared to 0°. At take-off angle 15° of La 3d photoelectron spectrum, binding energy position at La_2O_3 on carbon-glass substrate (855.6) was higher than 0° (854.0) 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 15° take-off angle was mainly contributed by photoelectron from La_2O_3.

Table 1. A comparison at La 3d component between take-off angle 0° and 15°.

Take-Off Angle	Binding Energies Position (ev) on Carbon-Glass Substrate			
	La_2O_3	$La(OH)_3$	La_2O_3	$La(OH)_3$
0°	834.2	837.1	850.4	854.0
15°	835.9	839.1	852.5	855.6

CONCLUSION

Surface adhesion study of La_2O_3 deposited on carbon-glass substrate was successfully done. From this work, several conclusions could be summaries as followed:

i. There were two types of oxide species on the substrates which were La_2O_3 and SiO_2.
ii. The oxide components that contribute to O 1s photoelectron were SiO_2, bulk, La_2O_3 and OH^- (water vapour).
iii. The chemical bonding formation between the La metal deposited and the surface was due to a chemisorption and physisorption process.
iv. A successful observation of La_2O_3 adhesion property on carbon-glass substrate was clearly seen from the O 1s binding energy from La_2O_3 component.
v. 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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