Characterisation of the oxide effects on aluminium opacity targets

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Abstract. 900 nanometre thick aluminium strips were produced by the Target Fabrication Group for an experiment at the Central Laser Facility. They were specified to be supported horizontally at either end across an 800 micron void and to be 500 microns in height. The production method used a Parylene (C₈H₈) supporting layer which was removed by oxygen plasma etching. This process resulted in a problematic contaminant layer that caused substantial increase to the absorption of X-rays in the laser campaign. The contaminant layer was characterised by optical microscopy and Scanning Electron Microscopy. Energy Dispersive X-ray Spectroscopy was able to detect a high relative abundance of carbon and oxygen in the plastic etched strips when compared to control samples. It has been shown that partially etched Parylene can form carboxylic groups with a ratio of 4:1 carbon to oxygen atoms. This effect was observed and exacerbated by the sample geometry not in sufficient contact with the grounded chamber baseplate causing charging and therefore insufficient hydrogen abstraction in the plasma. An alternative production method produced strips that were not as flat over the open area as the previous method but had no significant contaminant layer. This process involved coating a release layer of sodium chloride before the aluminium strips. When lowered into water, the salt dissolves in water and the strips are suspended on the surface tension, allowing the strips to be picked onto the mount. Each target required measuring for form using a white light interferometer where around half were within specification.

1. Introduction
This paper presents analysis of an aluminium strip target made by the Target Fabrication Group at the Central Laser Facility (CLF). The production method is outlined alongside characterisation data of the foil flatness and relative abundance of contaminants present on the surface. An alternative production method is presented to reduce contaminants and its suitability is discussed.

Techniques used to make the strip include coating plastic by Chemical Vapour Deposition, Aluminium coating by Physical Vapour Deposition and oxygen plasma etching; analysis techniques include Light Microscopy with Dark-Field Illumination, Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy and White Light Interferometry. All resources used are part of the Target Fabrication capabilities at the CLF.
1.1. Target Specification
An experimental campaign undertaken in January 2017 on the Vulcan laser system required targets of aluminium 900nm thick, 500µm high free-standing over a frame with 800µm gap. The form of the strip was specified to be as flat as possible and have no angles greater than 5 degrees with respect to the mount plane. A sketch of the design is shown in Figure 1.

2. Initial manufacture method
In order to easily place and support an Aluminium strip whilst also achieving flatness across the area the chosen manufacture method included supporting the strip with a plastic under layer that was removed by oxygen plasma etching.

2.1. Strip manufacture
A coating of Parylene N (trade name for a variety of chemical vapour deposited poly(p-xylene) polymers) of thickness 5 microns was deposited onto a standard microscope slide by Chemical Vapour Deposition. The microscope slide is then coated with the desired thickness of aluminium by thermal evaporation in a thin-film deposition plant. The “strip” width of 500µm was defined by using a mask made of 100µm thick photo-etched copper. Placing the mask flat down onto the Parylene coated microscope slide allowed for a coating with little shadowing as tested by a surface profilometer. The deviation in thickness coated across a microscope slide is considered well within reasonable error margins (±5% deviation from total thickness).
Figure 2. Strips of Aluminium coated through the copper mask onto a microscope slide. The strip edges were well-defined with little shadowing

Figure 3. Touch probe scan of the step height across a strip as shown in Figure 2. The difference of the two “L” and “R” zones measures 1.079(±0.064µm) and this is taken to be the thickness of the coating. The amount of shadowing in coating can be measured by looking at the quality of the “top-hat” profile

The touch probe scanned across the width of each strip and resulted in the scan in Figure 3. This profile measurement also serves as the thickness measurement for the coating run.

2.2. Oxygen plasma removal of plastic

Individual strips are cut from the slide manually using a scalpel and glued over the open area of the mount using a small amount of epoxy glue. This is placed inside a Plasma-Enhanced Chemical Vapour Deposition plant where oxygen plasma removes plastic by Hydrogen abstraction[1]. A flow rate of 30sccm oxygen is maintained at a pressure of 100mT by a gate valve to a turbo vacuum pump. A power of 150W is maintained by a discharge between two electrodes, creating plasma. This Oxygen plasma removes plastic at a rate of ~100nm/min. Choosing a time of >50minutes ablates ~ 5microns of plastic. This method has been verified by taking a control substrate (glass microscope slide) with plastic and etching under the same conditions. No remaining plastic is detectable by surface profileometry. The sample is then taken out and visually inspected to ensure all plastic is removed, the dimensions fit that of Figure 1 and there is no visible debris or deformity. The mount with the strip can then be placed onto a CLF standard aluminium post ready for laser irradiation in the target area.
The result using this production method yields a flat and reproducible strip that can be batch produced. When measured by Interferometry all targets were within specification and could be produced with high levels of consistency.

3. Alternative production method
The production method was chosen to remove any source of plastic and include no Oxygen plasma etching during processing.

3.1. Float off procedure
Firstly a release layer of sodium chloride was deposited on a substrate by way of Physical Vapour Deposition in a thermal evaporation coating plant. Then, using the same strip mask as in the first production method, aluminium is coated through the mask to define the strips onto the sodium chloride. When the substrate is lowered into de-ionised water the salt dissolves and the aluminium is released from the surface and is suspended on the surface tension of the water. The strip can then be lifted out of the water directly on to the steel target mount. This process was done manually by an experienced fabricator, it was labour intensive as each strip had to be processed by hand and produced varying results in terms of the flatness of the strip across the length.

3.2. Form measurement using White Light Interferometry
Each strip had its form over the open area measured to test against specification; White Light Interferometry gave a surface scan that allowed the form to be assessed. Due to the strict specified criteria for form around half of those produced were rejected. Figure 5 and 6 show an interferometry scan of the surface profile with a line-out across its length.
Figure 5. Interferometry of a target strip produced by float off. The interference fringes show the form of the strip

Figure 6. Resultant profile along the length of the strip, measured using a White-Light Interferometer. Note the scale is exaggerated. The strip falls 7 microns in the middle relative to the supported ends

4. Oxide observation by X-ray absorption

During the experimental campaign the users group noted an unexpectedly high X-ray absorption through the oxygen-etched sample strips, indicating there may be a much greater oxide layer than there would be natively in aluminium. Oxygen plasma can create a deep oxidation in Aluminium[5]. As a result, the user group took two identical shots: one on a standard production target and one produced via the alternative method. The results showed much greater X-ray absorption in the standard manufacture target, indicative of a thicker-than-native oxide layer. The X-ray absorption on the alternative produced target was considerably less and was characteristic of a native aluminium oxide layer.

The presence of the Oxide layer made the standard targets unsuitable for the rest of beam time. Target Fabrication undertook some retrospective characterisation research and chose the alternative production method for the remainder of the experimental campaign.

5. Contaminant characterisation

The produced strips were inspected with dark field and bright field optical techniques as well as Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDX) for contaminant quantities.

5.1. Optical Imaging

Figures 7 and 8 are optical images taken of the strips after etching. Figure 7 is a bright field image and figure 8 is a dark field image. Figures 7 and 8 clearly show plastic remaining around the strip despite prolonged etching.
Figure 7. Bright field image of Aluminium strip produced by production including a CH layer removed by Oxygen plasma etching. There is some plastic visible at the top and bottom.

Figure 8. Dark-field image of the strip. Dark-field microscopy excludes un-scattered light from the final image. Under dark field illumination plastic containment can be seen clearly in areas at the top and bottom.

5.2. Scanning Electron Microscopy (SEM) imaging

Imaging the extent of the plastic contaminant using optical microscopy is difficult due to its transparency but SEM allows imaging irrespective of optical properties.

Figure 9. Scanning Electron microscopy image of the same strip as figure 5. Plastic can be clearly seen around the strip.

Figure 10. Scanning Electron Microscope image of a strip produced by a method of “float off” this process includes no plastic coating or oxygen plasma processing. The strip is free of contaminants.

Figure 9 shows the extent of the remaining plastic. It is clear despite prolonged exposure to the Oxygen plasma it is not being removed fully. For comparison the below image (Figure 8) is a strip made by the alternative production method.

5.3. Identifying the contaminant using Energy Dispersive X-ray Spectroscopy (EDX)

Energy-dispersive X-ray spectroscopy of strips with contaminant and without contaminant; can be used firstly to; rule out considerable high-Z contaminant, and secondly, to give a relative abundance of carbon and oxygen content and estimate the extent of the contaminant. (Only relative abundance of low-Z elements can be obtained using EDX)
Using a beam of 5KeV and choosing an area of ~50µm² in the centre of the strip a 100,000 counts spectrum was taken. The results for the samples in Figure 9 and Figure 10 are in Tables 1 and 2.

### Table 1. EDX element data by relative abundance by weight and atomic number for a strip that had plastic removed by Oxygen plasma (Figure 9 and 10)

| Element | Weight % | Atomic % |
|---------|-----------|----------|
| Al K    | 53.29     | 37.31    |
| C K     | 27.52     | 32.50    |
| O K     | 19.19     | 30.19    |

### Table 2. EDX element data by relative abundance by weight and atomic number for a strip that had no plastic or plasma processing (Figure 10)

| Element | Weight % | Atomic % |
|---------|-----------|----------|
| Al K    | 76.24     | 60.99    |
| C K     | 8.27      | 11.16    |
| O K     | 15.49     | 27.84    |

Both the strips contained no detectable high-Z contaminant. Relative carbon content is far higher in the strips with the plastic coating that has been subjected to oxygen plasma. This shows that there is plastic remaining on the surface of the strip as well as around the edges. It also shows a slightly higher abundance of oxygen, this implies that the oxygen is reacting chemically with the carbon to form carboxylic groups, this has been show to occur in partially oxygen etched Parylene[1]. Carboxylic groups are resistant to further reaction with oxygen plasma which suggests why some plastic remained on the surface.

### 5.4. Modelling of electron interaction area and X-ray volume

To estimate a thickness of contaminant on the surface of the aluminium a CASINO was performed as shown in figure 11. CASINO software is a “Monte Carlo Simulation of electron trajectory in solids” specially designed for low energy electron interaction in a bulk and thin foil[2] CASINO calculates the electron trajectory by a series of separate scattering events, after which the electron is absorbed and energy is released as electromagnetic radiation. The depth of the electron “tear-drop” shape is dependent on a number of factors including density of material and starting electron energy. This technique has been used to estimate the thickness of thin film layers[3][4]. Using a simulated electron beam that is absorbed in a characteristic teardrop shape it is possible to analyse where electrons are absorbed and released as X-rays.

A 5KeV electron beam was modelled entering an Aluminium substrate with a Carbon/Oxygen contaminant on the surface. A 225nm contaminant layer of element ratios 4C:O:3H and density 1.06g/cm³ is modelled below. This ratio was chosen to represent Carboxylic acid. Different thicknesses of contaminant were trailed to match the EDX data, through trial and error; this could then be used to estimate the thickness. A 5KeV electron beam was modelled entering an Aluminium substrate with a Carbon/Oxygen contaminant on the surface. A 225nm contaminant layer of element ratios 4C:O:3H and density 1.06g/cm³ is modelled below. This ratio was chosen to represent Carboxylic acid. Different thicknesses of contaminant were trailed to match the EDX data, through trial and error; this could then be used to estimate the thickness.
Figure 11. A simulation of 5KeV electrons in a 225nm plastic contaminant containing a ratio of 4C:O:3H and a density of 1.06g/cm$^3$ on top of solid Aluminium. The teardrop shape shows where electrons are absorbed and reemitted as X-rays.

Table 3. X-ray yield for each element present in the simulation as a percentage of total

| Element | Weight % |
|---------|----------|
| Al K    | 57       |
| C K     | 27       |
| O K     | 16       |

Using a contaminant layer of 225nm in the simulation the abundance of element matches the data collected from the contaminated strip, suggesting the contaminant thickness is on this order of magnitude.

An EDX map of the strip would be advantageous however this was difficult to achieve because of the charging of the areas of plastic contaminant around the strip.

6. Conclusions

Self-supported Aluminium strips of 900nm in thickness and 0.5mm in width were batch produced by using a Parylene support film which were consistently flat across the open area as measured by interferometry. The oxygen plasma etch to remove the plastic support film introduced a contaminant layer of carbon and oxygen atoms which rendered them inadequate for experimental use. The contaminant layer was confirmed by EDX to be an abundance of carbon with some inclusion of oxygen.

Although chemical bonding could not be probed with the equipment it is theorised that the oxygen plasma chemically bonded with the plastic support layer and produced carbon-oxygen functional groups which were resistant to further etching. A 225nm 4:1 carbon-oxygen contaminant on the surface of aluminium was modelled under a 5KeV beam, the energy emitted as X-rays from each element was
comparable to data gathered from EDX of a contaminated strip. Increased contaminant occurred with these samples more readily than comparative samples because of the geometry of the sample in the plasma, poor conduction with the baseplate inside the process chamber caused the sample to charge.

As a result of problematic contaimant layers an alternative production was used. Coating the strips onto a release layer of sodium choride succeeded in producing a product with no significant contaminant, however, this was labour intensive and produced inconsistent flatness across the open area. The criteria for form required each one to be quality checked and only around half of those produced were suitable.

7. Further Work
To further analyze the surface chemical nature, X-ray photoelectron spectroscopy could be employed. This technique can be used to analyze the surface chemistry of a sample and would give insight into the oxygen containing functional groups present on the surface as a result of oxygen plasma etching.

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