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# Corrosion Resistance with Perfect Atomic Layers: An Introduction to CORRAL

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PLASMA & MATERIALS PROCESSING

SEVENTH FRAMEWORK PROGRAMME

## What is CORRAL?

A Europe-wide project investigating corrosion protection with perfect atomic layers.

## Primary Goal

To develop an efficient corrosion protection system comprising defect-free ultra-thin sealing coatings with excellent barrier properties.

## CORRAL Requirements

The current state of the art of films for corrosion protection is ~3 µm. The coatings developed in the CORRAL project should be:

- Ultra-thin (> 50 nm),
- Chemically inert material,
- An excellent sealant, which should be defect-free.

## Corrosion Resistance

Corrosion is the result of wear or chemical attack in mechanical moving parts. Forming a thin barrier layer will protect metallic components without dramatically altering their shape. As atomic layer deposition (ALD) affords thin films with excellent conformality over a large batch area,[1] its use as a route to corrosion resistant layers could be crucial.

## Low Temperatures

ALD is a method whereby thin films of a material can be deposited *via* cycles of pulsed precursor dosing and purging. The substrate temperatures typically range from 100-450 °C.[2] As the mechanical properties of the substrates can be altered by temperatures greater than 160 °C, the ALD process needs to be optimised under these conditions. There are few reports of depositions below 100 °C, the most notable being the ALD of $Al_2O_3$ from $[Al(CH_3)_3]$ and water[3] or ozone.[4] We are investigating the use of plasma-enhanced ALD as an alternative to these routes to see if high quality films can be obtained at such low temperatures.

## Substrates

**Silicon**
With a monolayer of $SiO_2$ (process optimisation)

**Steel (100Cr6)**
'Conventional' steel

**Stainless Steel (316L)**
Stainless attribute due to 18-20% chromium

**Aluminium 2000**
A standard aluminium alloy

## Plasma-Enhanced ALD of $Al_2O_3$

Plasma-enhanced atomic layer deposition was used to deposit 10 and 20 nm of $Al_2O_3$ onto the steel and aluminium substrates. The precursors were trimethylaluminium (TMA) and an oxygen plasma (the cycle is shown in Fig. 1). The two half reactions are:

1. $\text{Al–OH*} + [\text{Al(CH}_3)_3]_{(g)} \rightarrow \text{Al–O–Al(CH}_3)_2\text{*} + \text{CH}_{4\,(g)}$
2. $\text{Al–CH}_3\text{*} + 4\,\{\text{O}\} \rightarrow \text{Al–OH*} + \text{CO}_{2\,(g)} + \text{H}_2\text{O}_{(g)}$

* Denotes a surface-bound species.

The temperatures investigated were 50, 100 and 150 °C. A thermal ALD process was also run at 150 °C for comparison.

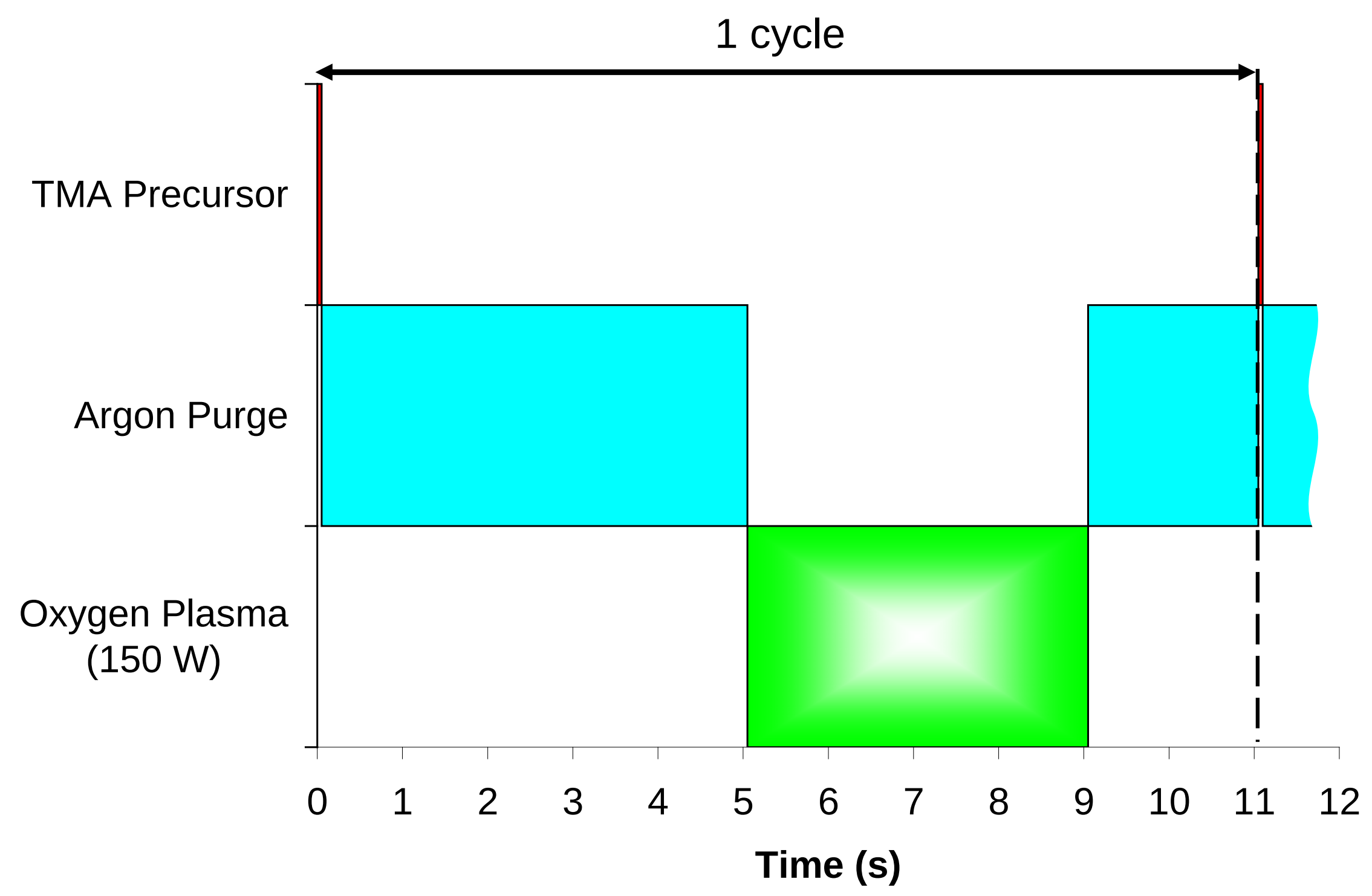

**Figure 1.** A cycle for plasma-enhanced ALD of $Al_2O_3$.

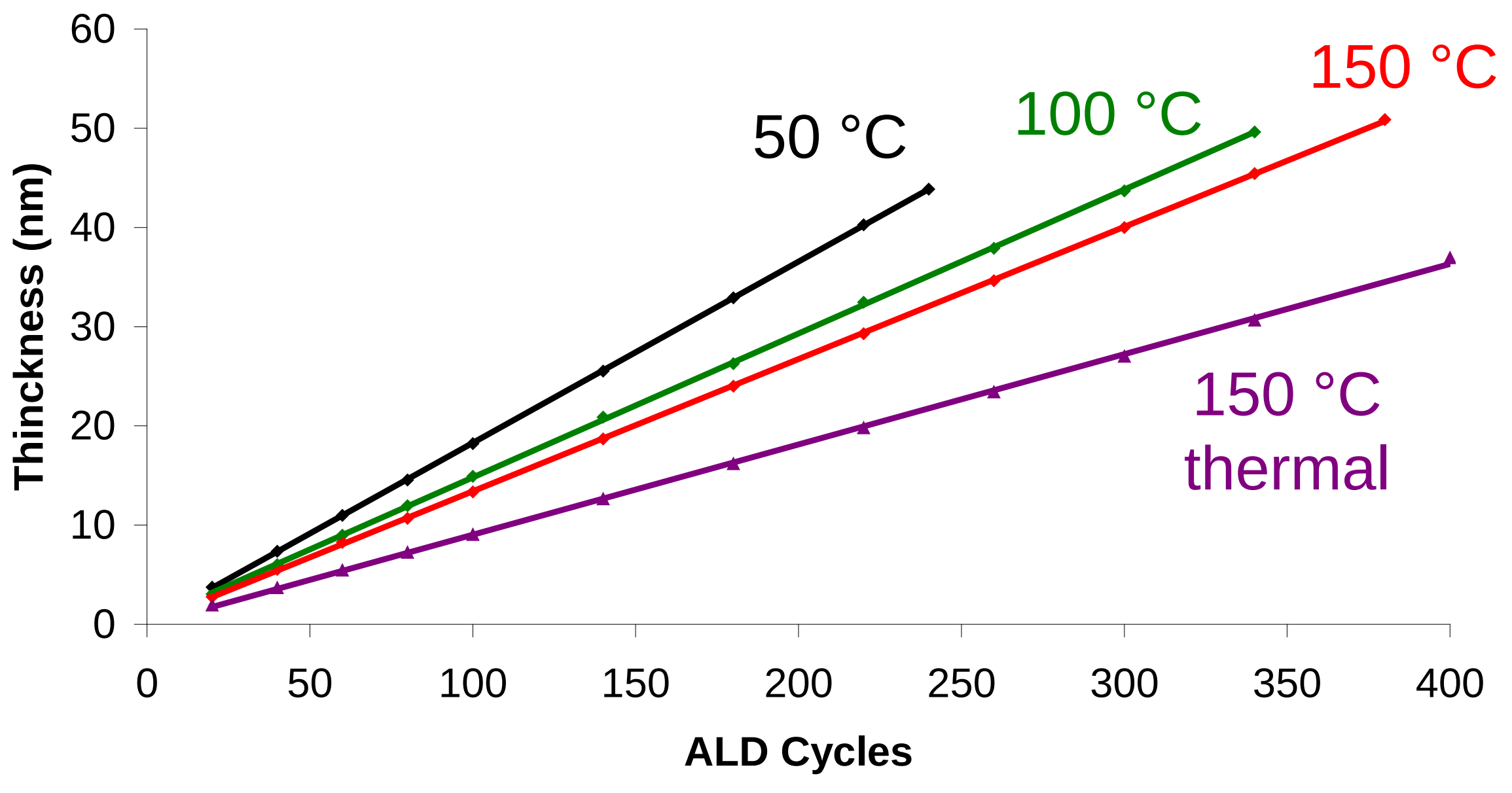

**Figure 2.** Temperature series of films, showing how the growth rate is dependent on deposition temperature.

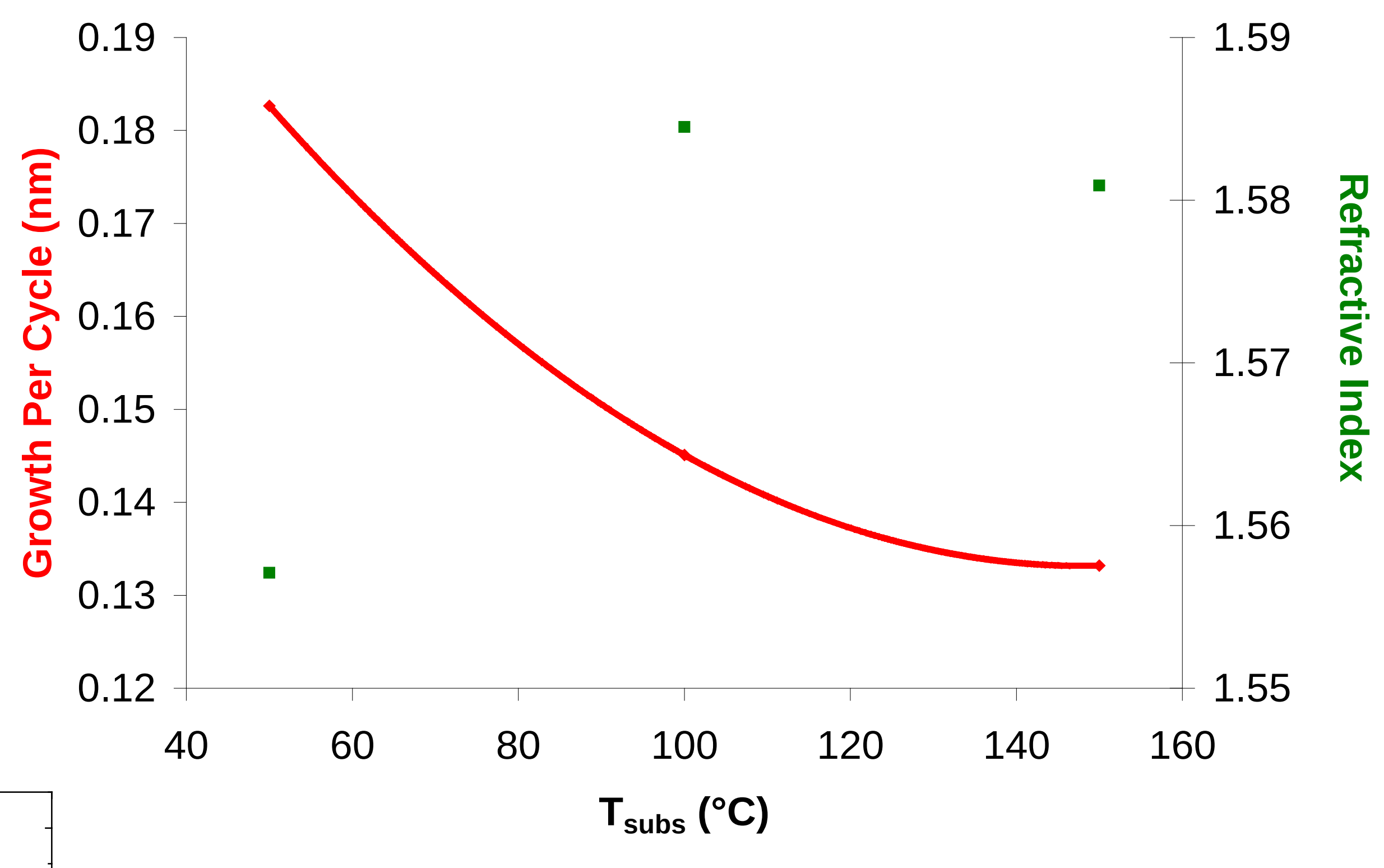

**Figure 3.** Variance of growth rate and refractive index with deposition temperature ($T_{subs}$) for 10 nm films.

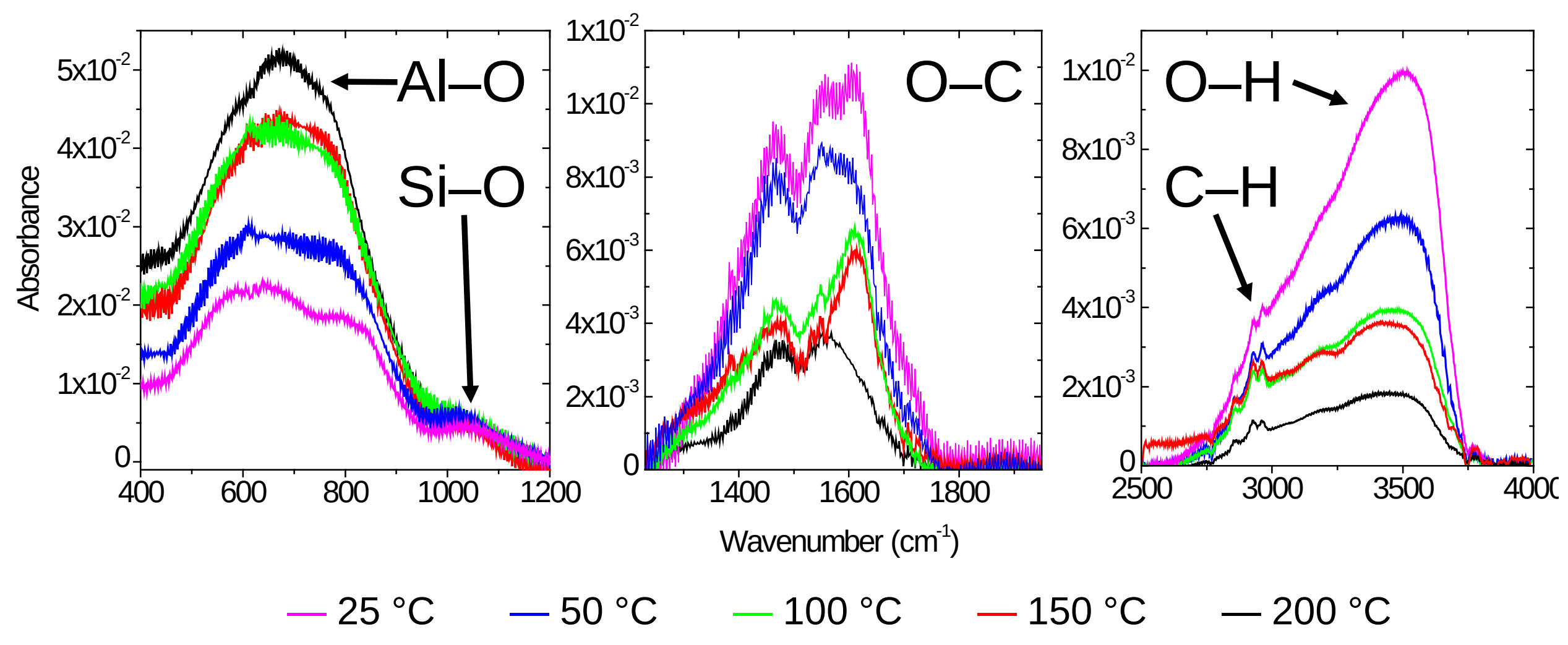

**Figure 4.** FT-IR spectra of the films on Si{100}. The regions shown are for Al–O, C–O and C–H and O–H respectively.

## Results

The growth rate per cycle was highest at lower deposition temperatures for the plasma-enhanced process (Fig. 2 and 3), due to the formation of water in the plasma step. This was confirmed by the greater intensity of –OH peaks in the FTIR spectra (Fig. 4) at lower temperatures.

The thermal process at 150 °C afforded a lower growth rate as the reactivity of water at this temperature is lower than that of the plasma.

The refractive index of the films deposited at 50 °C was significantly lower than for the other temperatures, suggesting that these conditions give films of a lower density, possibly as a result of hydroxyl impurities.

## Summary

Thin films of $Al_2O_3$ have been deposited on steel and aluminium substrates at temperatures ≤ 150 °C, which will be tested for corrosion resistance. The impurities in the films decreased with increasing temperature, as did the growth rate per cycle.

## References

1. R. Matero, M. Ritala, M. Leskelä, T. Salo, J. Aromaa, O. Forsén, *J. Phys. IV*, 1999, **9**, Pr8: 493.
2. J. Niinistö, M. Ritala, M. Leskelä, *Mater. Sci. Eng. B*, 1996, **41**, 23-29.
3. M. D. Groner, F. H. Fabreguette, J. W. Elam, S. M. George, *Chem. Mater.*, 2004, **16**, 639-645.
4. S. K. Kim, S. W. Lee, C. S. Hwang, Y.-S. Min, J. Y. Won, J. Jong, *J. Electrochem. Soc.*, 2006, **153**, F69-F76.

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