Evidence of Chemical Complexity and Laser-Driven Autocatalysis in Type IA FBGs

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Abstract: We observe the first chemical complexity for Type IA FBG growth under prolonged UV laser exposure. Out-of-phase oscillatory behaviour in GeOH/SiOH formation provides evidence of laser-driven autocatalysis and chemical origins for grating formation.
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1. Introduction and experimental results

Type IA or Type 1*p* fibre Bragg gratings (FBG) are formed in hydrogenated germanosilicate fibres at room temperature [1, 2], as combined hydrogenation and UV-laser fluence conditions induce local material changes that lead to large increases in the Bragg wavelength (λ_{Bragg}) and mean index (Δn_{eff}) of the fibre core during FBG inscription (Fig. 1). The modulated index change (Δn_{mod}) shows oscillatory growth behaviour and the overall grating growth (the increase in $\Delta\lambda_{Bragg}$) is correlated with absorption features that appear at ~1400nm linked to the formation of both SiOH and GeOH groups, Fig. 1 [3]. For highly doped fibres (Ge or B/Ge) $\Delta\lambda_{Bragg}$ ~15–20nm, translating to an increase in the effective core index of $\Delta n_{eff} \sim 2\text{x}10^{-2}$ [4]. We believe that these index modifications must reflect material changes within the core and core-cladding regions, consistent with net structural relaxation and hence stress changes at the core-cladding interface. The extraordinarily large laser fluence further supports an annealing-like relaxation. Such changes can exceed the local polarisability changes around altered or induced microscopic defect sites alone. Given that the formation of SiOH and GeOH species can provide an indication of net energy imparted to the network, high temperature thermal annealing can lead to auto-oscillatory behaviour as hydrogen out-diffuses [5]. In recent studies we did not observe this in Type IA FBG formation in Ge-doped fibre suggesting that the inscription temperatures (between 100 and 200°C) induced by UV excitation and UV-induced bond breaking proved ineffective and concluded that auto-oscillatory catalysis did not occur [6]; new data analysis show conclusively otherwise.

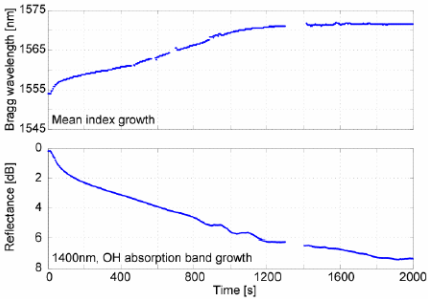


Fig. 1. Mean index change (or IA maturity) and the 1400nm absorption band under UV exposure.

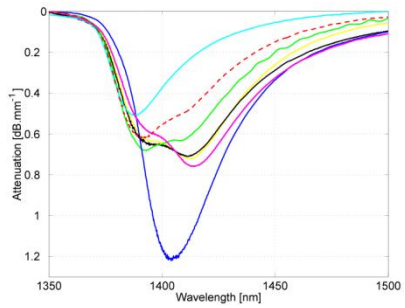


Fig. 2. (a) OH bands created in the optical fibres, partially listed in Table 1, by uniform exposure to UV radiation.

Table 1. Summary of the absorption band peaks and dopant levels for the fibres tested. U – Unidentified.

Fibre reference	Manufacturer	Fig. 2 colour convention	Fibre type	Main peak		Secondary peak	
				nm	dB/mm	nm	dB/mm
SMF28	Corning	Cyan	STD	1388	0.51	U	U
PS1250/1500	Fibercore	Blue	B/Ge	1404	1.22	1425	U
SD079-00B	Fibercore	Green	Ge	1393	0.68	1408	0.63

We propose that if coupling exists between SiOH and GeOH, their absorption bands will oscillate *out of phase*, and follow an exponential decay profile as free OH or H hops between sites and slowly diffuses out of the fibre core. For this to occur, there must be an equivalence between GeOH and SiOH free energies that is achieved when their free

energy of formation is lower than the surrounding energy bath of the network. At room temperature this is impossible and temperatures above 500ºC are necessary [5]. As the effective temperature is ~100ºC, UV laser induced bond breaking would have to reduce the energies of Ge and Si sites to allow much lower phonon energies to release OH or H, with index linked to differences between the index polarisability at the GeOH and SiOH sites.

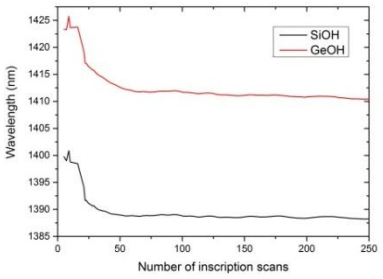
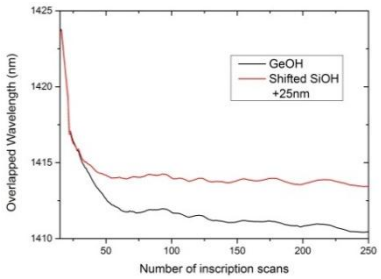
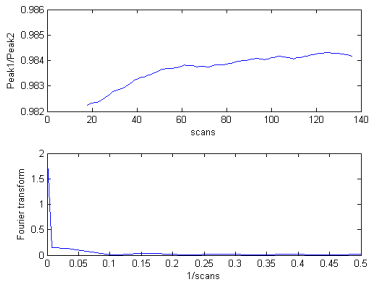


Fig. 3. (a) Evolution of SiOH and GeOH absorption band peak wavelengths with laser scan number – *NCC*.



(b) Superimposed SiOH/GeOH curves to compare growth and equilibrium with laser scan number – *NCC*.



(c) Ratio of SiOH/GeOH absorption band peak wavelengths vs scan number and their FFT, excl out-of-phase oscillations – *NCC*.

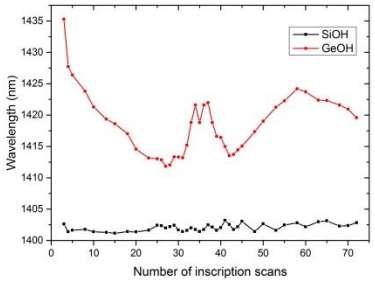
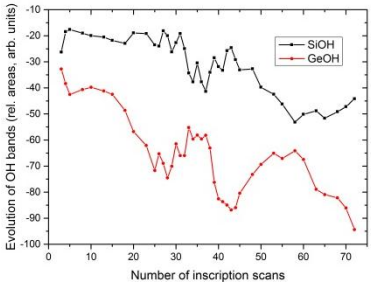
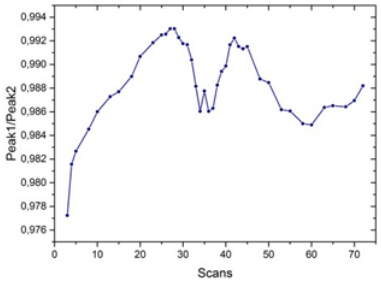


Fig. 4. (a) SiOH and GeOH absorption band peak wavelengths vs laser scan number – *CC*.



(b) Evolution of SiOH/GeOH absorption band areas with laser scan number – *CC*.



(c) Ratio of SiOH/GeOH absorption band peak wavelengths vs scan number – *CC*.

Fig. 3 shows there are no chemical complexity (*NCC*) and autocatalysis processes for Ge-doped fibre (SD079-00B), despite the role of OH in the large dc shift and possible role as a photorefractive component generating the low thermal stability of the modulated index. Clearly the background energy is too low to equalise the energy levels of the general GeO and SiO bond sites for OH formation. The combined UV bond breaking and effective heating are unable to provide this energy. However, the B/Ge codoped fibre (PS1250/1500) does show that autocatalysis *is present* and *contributes* to Type IA grating formation (Fig. 4); the changes are observed to be out-of-phase as anticipated and consistent with a diffusion-mediated hopping process. The observed index modulation is a reflection of the exchange between the OH species, clearly showing the presence of chemical complexity (*CC*). This exciting new development shows the importance of dopants in fine tuning chemical complexity within an optical fibre offering unprecedented control over the final index stability. This marks a major scientific milestone, establishing the topical waveguide as an exciting new platform for complexity studies including chaotic material behaviour.

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3. References

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