Thermal Decay of Fibre Bragg Gratings of Positive and Negative Index
Changes Formed at 193 nm in A Boron-codoped Germanosilicate Fibre

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Abstract: A complex grating decay process is observed at elevated temperatures as predicted by a recently proposed three energy level model. We have also measured thermal stability of fibre gratings of both positive and negative index changes in a Boron-codoped germanosilicate fibre in order to characterise the energy levels of the system and to predict of grating lifetimes. The negative index gratings are found to be able to operate at 300°C for over 25 years without significant degradation.

Key words: fibre Bragg gratings, fibre photosensitivity, decay of gratings
Background

The field of photosensitive fibre Bragg gratings has progressed enormously over the last few years. The effect has proven to be a complex phenomenon. A good understanding of the process is much needed for the rapid progress of the field. In a recent paper [1], we have attempted to propose a three energy level system (TEL), supported by the observation of I) a slower negative index change following the initial positive index change, II) the growth rate of the index change being proportional to the intensity of the writing beam, and III) the saturated index change being independent of the intensity of the writing beam. We have used the TEL model to successfully predict the grating growth and to explain the amplification of gratings with a subsequent uniform exposure. We have also found that, similar to those written at ~240 nm [2], the negative index change is much more stable than the corresponding positive index change. In this paper, we report a study of thermal decay process in fibre Bragg gratings formed at 193 nm in a boron-codoped germanosilicate fibre to confirm the predications of complex decay process from the TEL model and also to quantify the details of the TEL model energy levels.

Complex Grating Decay

In the TEL model, level 2 (see fig.1) is populated by depleting a ground level (level 1) and then quickly relaxed into level 2a to give a positive index change. A negative index is created by populating level 3a from level 2a via a similar process. We do not deal with the microscopic details of the levels here, which have been the
subjects of many publications [see for example 3,4]. The energy barrier for population at level 3a to relax is much higher than that for level 2a, this makes the negative index changes more stable. If a grating is formed with both level 2a and 3a populated, a complex thermal decay process is expected for the gratings where the positive index change decreases first and then followed by the negative index change. Since the grating total index change is a sum of the two effects. The grating is expected to grow when heated if it is dominated by negative index change and verse versa. We have studied this effect with various population distributions at level 2a and 3a. The population distributions were achieved by terminating the grating growth at different stages of the writing process. The results are shown in fig.2 with the growth curve plotted in the inset to indicate the relevant writing time.

The growth takes ~30 mins to complete when writing at 193 nm at ~0.3 J/cm² and 10 Hz, much faster than when writing around 240 nm [2]. A boron-codoped germanosilicate fibre was used in this study together with a phase mask supplied from QPS Technology Inc. When a grating is formed with predominantly level 2a populated, a simple decay is expected (see grating A in fig.2). A grating length of 1 mm was used to ensure uniformity of the gratings. As the population in level 3a increases (see grating B), the grating will decay to zero when the level 2a population decreases just enough to balance the negative index change, this happening at ~300°C for grating B. Beyond this point, the grating is formed by an overall negative index change and is expected to increase when the level 2a population decreases further (see grating B at 400 °C). This effect is much more obvious for grating C when such a balance between the positive and negative index
changes was achieved at the beginning of the decay process (there is almost no grating in the fibre when written). For the overall negative index gratings (D and E), the decrease in level 2a population at lower temperature, will cause the grating to grow until the level 3a population starts to decrease. For grating F when the population is mainly in level 3a, hardly any decay was observed until 300 °C.

Grating Decay Theory

By studying the thermal decay of gratings with just level 2a or level 3a populated, we will be able to quantify the decay barriers for both positive and negative index gratings. This is very important for predicting grating life time and the amount of pre-annealing required to achieve certain required grating life time.

A comprehensive decay model has been proposed by Erdogan [5] using a combination of experimental data and reasoning. The author has however arrived at a method which is difficult to use when analysing experimental data. Here we try to derive the same fundamental results via a simple mathematical model, so that the error of the approximations can be quantified and analyse of experimental data can be easily conducted. Thermal decay of a population $g(E,t)$ as a function of barrier energy $E$ and time $t$ at trapped sites from an initial population $g_0(E)$ can be generally expressed as:

$$g(E,t) = g_0(E) e^{-\nu(E)t}$$

(1)
where with $k_B$ being Boltzmann constant and at temperature $T$ (K)

$$\nu(E) = \nu_0 e^{-E / k_BT}$$  \hspace{1cm} \text{(II)}$$

The total remaining population at all barrier energy sites $N(t)$ is therefore:

$$N(t) = \int_0^\infty g_0(E) e^{-\nu_0 t} e^{-E/k_BT} dE$$  \hspace{1cm} \text{(III)}$$

If the initial population distribution is signification broader than $k_B T$ (0.09 eV for $T=800^\circ C$) then:

$$e^{-\nu_0 t e^{-E/k_BT}} = 0 \text{ when } E < E_d$$

$$e^{-\nu_0 t e^{-E/k_BT}} = 1 \text{ when } E > E_d$$  \hspace{1cm} \text{(IV)}$$

where

$$E_d = k_B T \ln \frac{\nu_0 t}{\ln 2}$$
$E_d$ is the demarcation energy below which all the population has decayed and above which population has not been touched. As we will see later, the condition that the initial population distribution is significant larger than $K_BT$ is normally satisfied. Once we have assumed a Gaussian distribution centred at $E_0$ for an initial population, $g_0(E)=\exp(-(E-E_0)/\Delta E)$, the normalised total remaining population $n(t)$ can be written as:

$$n(x)=1-\frac{1}{\sqrt{\pi}} \int_{-\infty}^{x} e^{-w^2} dw$$

(V) 

where $x=(E-E_0)/\Delta E$. $n(x)$ is plotted in fig.3 together with a stretched exponential \[ \exp(-\ln 2 \exp(1.678x))=\exp(At^\alpha) \] and power law $1/(1+\exp(2.4x))=1/(1+At^\alpha)$. The power law fit offers much better approximation to $n(t)$ with

$$\alpha=2.4\frac{k_BT}{\Delta E}$$

$$A=e^{-2.4E_0/\Delta E} e^{(2.4/\Delta E)\ln(\nu/\ln 2)} k_BT$$

(VI)
The power law fits well apart from some deviation at the beginning and the end of the decay, $\alpha$ shows a linear dependence on $T$ and $A$ an exponential dependence. These dependence have been found by Erdogan. Here we established the simple relations between the measured $A$ and $\alpha$, and the distribution parameters $E_0$, $E$ and $\nu_0$. Using the parameters give by Erdogan in [5] for an erbium-doped germanosilicate fibre using a writing wavelength of 242nm, $\alpha=T/5250$ and $A=1.86 \times 10^{-3} \exp(7.64 \times 10^{-3} T)$, we obtain $E_0=2.8$ eV, $\Delta E=1.08$ eV (FWHM=1.8 eV) and $\nu_0=2.5 \times 10^{15}$ Hz, comparing well with the same parameters given in the paper, $E_0=2.8$ eV, FWHM=1.6 eV and $\nu_0=1.9 \times 10^{15}$ Hz. In [6], thermal decay of gratings written in a boron-codoped germanosilicate by a frequency quadrupled NA:YLF laser at 262 nm was measured, giving $\alpha=T/1667$ and $A=5.98 \times 10^{-6} \exp(7.64 \times 10^3 T)$. The population distribution parameters can be given as $E_0=1.7$ eV, $\Delta E=0.34$ and $\nu_0=3.3 \times 10^{-3}$ Hz. The bandwidth $\Delta E$ in this case is much smaller than in the previous example, but it is still much larger than $K_B T$ to valid the approximation for equation IV.

Decay of Gratings with Positive Index Changes

Thermal decay for level 2a was performed with gratings exposed for $\sim 30$ seconds to ensure that level 3 is not significantly populated (see inset in fig.4 for the relative position in the growth). As for weak gratings ($\kappa L<0.5$), total reflection from a grating is proportional to $(\kappa L)^2$. For the experiment in fig.4, the gratings were $(18\pm3)\%$ reflectivity. This is equivalent to $\kappa L=0.42$. Total reflection was monitored and then converted into normalised $\kappa$. A broadband LED source in combination with a 3dB
coupler was used for the measurements. A well characterised tube furnace is heated to a desired temperature first before a grating is quickly loaded into a predetermined point in the furnace.

The results together with the power law fittings are shown in fig.4. The power law fits well apart from few data points at the beginning of each decay curves (note that the time axis is plotted in logarithm to show clearly the decay at the beginning and the decay starts at t=1 min). This is probably due to some preannealing when gratings were written and the small misfit expected at the beginning and the end of the decay from fig.3. A and \( \alpha \) are plotted as a function \( T \) in fig.5 and 6 respectively. \( A \) and \( \alpha \) are found to fit \( 0.00173e^{0.00824T} \) and \( 0.0153e^{0.00575T} \) respectively. \( A \) fits well with an expected exponential fit. \( \alpha \), however, deviates substantially from a linear relation to \( T \) as derived earlier. The fitting error for all the data in fig.5 and fig.6 is less than 5\% which is insignificant to explain the misfit. The main error came from the repeatability of the measurements. The magnitude of this error can be seen from the repeated measurements at \( T=573 \) K and \( T=873 \) K in fig. 5 and fig. 6. This error is not significant either to explain the discrepancy. A distribution other than Gaussian will affect decay both at low and high temperatures. This discrepancy must come from a secondary effect which makes the decay at higher temperature faster than what is predicted by the theory given before. We do not have a valid explanation for what this secondary effect may be. One possible explanation may be that there is an additional decay caused by photons generated in the furnace when operating at high temperature. This effect will increase with temperature. It should be taken into considerations while calculating distribution parameters for grating life.
prediction at low temperature using data obtained from decay test at very high temperatures. Otherwise decay measurements at low temperatures should only be used. We use only the measurements below 600 K in fig. 5 and 6 for the calculation of the distribution parameter. The measured \( \alpha \) in fig. 6 below 600 K fit well with a straight line, \( \alpha = T/2200 \) (see fig. 6). We still use the fitting for \( A \), \( A = 0.00173e^{0.00824T} \), as it fits well with the data at lower temperatures. From the relations given in the last section, it is easy to calculate the distribution parameters, \( \Delta E = 0.45 \text{ eV}, E_0 = 1.2 \text{ eV} \) and \( v_0 = 7.2 \times 10^5 \text{ Hz} \). This parameters are close to similar parameters obtained in last section for a similar boron-doped germanosilicate fibre with a grating writing wavelength of 262 nm.

Decay of Gratings of Negative Index Changes

An accurate stability measurement of the level 3a gratings is much more difficult to obtain, as there is always some non-zero population in level 2a. Even worse is the fact that at the trough of the writing fringe, the fibre is exposed to less fluence than that at the peak. Therefore, the proportion of level 2 population varies from one part of the grating to another. To ensure that the gratings consist of mostly negative index changes, we stop the grating growth when it is well into saturation of the second growth (see inset of fig. 7). A thermal stability test for gratings written with \( \sim 30 \) minutes of exposure is shown in fig. 7. The gratings were 0.5 mm long and (17±3)% reflection to ensure \( kL < 0.5 \). The decay at the beginning of each curve shows some abnormal decay, possibly affected by the decay of the small amount of level 2 population. The relatively stable nature of the negative index change is
obviously shown in fig.7, particularly at lower temperatures. The A and \( \alpha \) are again found to better be fitted with exponentials \( A=3\times10^{-10}\exp(2.7\times10^{-2}T) \) and \( \alpha=3.9\times10^{-5}\exp(1.29\times10^{-2}T) \) (see fig. 8 and fig.9). The measured data for A is quite scattered due to the presence of some positive index changes. We use only the \( \alpha \) measurements below 750 K for our calculation. A linear fit to the measured \( \alpha \) below 750 K gives \( \alpha=T/2900 \). Using this linear fit and the exponential fit to the measured A, we obtain \( \Delta E=0.6 \) eV, \( E_0=5.5 \) eV and \( \nu_0=1.3\times10^3 \) Hz.

**Discussions and Conclusions**

Using the distribution parameters obtained from last two sections, we will be able to predict the lifetimes of the gratings simply by using

\[
n(t) = \frac{1}{1+e^{2A(E_f-E_c)/\Delta E}}
\]

(VIII)

where \( E_f=K_0T\ln(v_o/\ln2) \). It is also very easy to calculate the lifetimes of preannealed gratings. In this case, accumulated decay is calculated at two different temperatures. Such calculations are shown in fig.10 (note the logarithmic horizontal axis and the start of decay at \( t=1 \) year). A position index change is expected to decay by \( \sim30\% \) at 80°C for a period of 25 years and a negative index change will hardly decay during the same period. At 300°C, the negative index change will only decay by \( \sim3\% \) in 25 years time. After a preannealing at 400°C for 30 minutes, the negative index change will hardly change over a period of 25 years after an initial
decay of \(\sim 4.5\%\). This type of highly stable gratings is especially suitable for sensor applications where operation at high temperature for excessive long time is required.

To summarise, we have studied the stability of both positive index gratings and negative index gratings at elevated temperatures. The measured distribution parameters allow us to predict the grating lifetimes. The negative index grating is proved to be able to operate at 300\(^\circ\)C for much over 25 years of operation life without significant deterioration.
Reference:


Figure Captions:

Figure 1 The schematic diagram of the three energy level system.

Figure 2 Decay of gratings with varying levels of positive index and negative index changes.

Figure 3 The remaining population $n(x)$ and its stretched exponential and power law fittings.

Figure 4 Decay of gratings formed mainly by positive index changes at different temperatures and power law fittings to the decay.

Figure 5 Power law parameter $A$ for the positive index change gratings against temperature $T$.

Figure 6 Power law parameter $\alpha$ for the positive index change gratings against temperature $T$.

Figure 7 Decay of gratings formed mainly by negative index changes at different temperatures and power law fittings to the decay.

Figure 8 Power law parameter $A$ for the positive index change gratings against temperature $T$.

Figure 9 Power law parameter $\alpha$ for the positive index change gratings against temperature $T$.

Figure 10 Prediction of grating lifetimes.
Figure 1
Figure 2

The graph shows the normalized total reflection as a function of time for different temperatures. The x-axis represents time in minutes, ranging from 0 to 140, while the y-axis represents the normalized total reflection, ranging from 0.0 to 1.4. The graph includes lines labeled A, B, C, D, E, and F, each corresponding to a different temperature: 100°C, 200°C, 300°C, 400°C, 500°C, and 600°C. The temperature scale is indicated at the bottom of the graph.
Figure 3
Figure 5

The graph shows a plot of absorbance (A) against temperature (K) with the following equation:

\[ 1.73 \times 10^{-3} \exp(8.24 \times 10^{-3}T) \]

The data points represent measured absorbance values at different temperatures.
Figure 6

- Measured data
- \(1.53 \times 10^{-2} \exp(5.75 \times 10^{-3}T)\)
- \(T/2200\)
Figure 7
Figure 8

A

O measured data

3X10^-10Exp(2.7X10^-2T)

Temperature (K)
Figure 9
The graph shows the normalized index change over time for different conditions.

- **Positive index change at 80°C**
- **Negative index change at 80°C**
- **Negative index change at 300°C**
- **Negative index change preannealed at 400°C for 30 mins then at 300°C**

The y-axis represents the normalized index change, ranging from 0.4 to 1.1. The x-axis represents time in years, ranging from 1 to 100.