Fluorescence of Ti^{3+} ions thermally diffused into sapphire

L M B Hickey, E Martins, J E Román, W S Brocklesby and J S Wilkinson

Optoelectronics Research Centre

Abstract

The thermal diffusion of Ti^{3+} ions into sapphire is demonstrated and the spectroscopic characteristics of the locally-doped region are presented. The spectral lineshape, polarisation dependence and the excited-state lifetime of indiffused Ti:sapphire are in excellent agreement with previously published data for high quality, bulk doped Ti:sapphire laser crystals. An order of magnitude estimate of the diffusion coefficient at 1950°C is D = 10^{-14} m^{2}s^{-1} These results represent a significant step in the development of a versatile broadly tunable waveguide laser based on the Ti^{3+}:sapphire material system established for conventional bulk lasers.

The rapid growth in integrated optical and optical fibre technology has led to increased demand for versatile, compact laser sources. Waveguide laser systems in both fibre and planar geometries have been demonstrated, but most of these are based upon transitions of rare earth ions doped into either glass or crystalline hosts. For integrated optical devices, crystalline hosts are of particular interest since any non-linear properties may be exploited in the design of both active and passive components. For example, in a LiNbO$_3$ host, numerous monolithic waveguide devices have been reported, such as Q-switched[1] and wavelength tunable[2] lasers. In general, such rare-earth-doped devices exhibit gain over a narrow wavelength range and thus have limited tunability.

The development of a broadly tunable waveguide laser would offer a convenient, compact versatile light source with applications in sensing and spectroscopy, and with the potential to be pumped by a miniature solid-state source. In the near infra-red regime, an attractive candidate is a waveguide laser based on the well-known bulk optic Ti:sapphire system. Continuously tunable from 660nm to 1100nm, the Ti:sapphire laser has rapidly become established as a leading broadly tunable solid state radiation source. The realisation of a versatile waveguide laser system in sapphire requires both the development of optical waveguides and the local introduction of the active ions in the sapphire substrate.

Bulk crystal optical gain media are typically based on synthetically grown single crystals, bulk doped with the active ion during the growth process. For integrated optical devices, which exploit planar lithographic processing, it is advantageous to locally define the distribution of optically active centres to regions coincident with the appropriate waveguide components. In principle, this enables the design of highly versatile waveguide circuits incorporating both active and passive devices within the same substrate host. For example, in the development of a Ti:sapphire waveguide laser the local introduction of the Ti^{3+} active ion may allow the eventual integration of undoped pump multiplexers and wavelength tuning devices. Additional advantages of this approach are that standard, low-cost, high quality, undoped sapphire wafers may be employed as the base substrate material and that the titanium dopant concentration and distribution may be varied spatially along the waveguide. The latter introduces a flexiblity of device length and titanium concentration which may be optimised to eliminate some of the heating problems associated with bulk laser systems.

Thermal indiffusion presents an attractive technique for locally introducing impurity ions in the preparation of an integrated optical device. In order to exploit the potential of the indiffusion process to allow control over both the spatial distribution and concentration of the dopant, the diffusion characteristics must be determined. Limited data is currently available describing the diffusion of transition metal ions in sapphire; however the reported lattice diffusion rates for transition metals similar to Ti, for example Cr, Ni and Fe, indicate that mass transport rates are prohibitively low unless diffusion temperatures approaching the melting point of sapphire are used[3].

In this Letter, the thermal indiffusion of titanium into sapphire is reported for the first time, and the spectroscopic properties of the localised Ti-rich region are described. These results clearly indicate that a significant proportion of the Ti has been incorporated in a lattice site and valence state that gives rise to optical characteristics comparable to that of a high quality bulk-doped Ti:sapphire laser crystal.

The spectral characteristics of a bulk doped Ti:sapphire crystal are well known[4]. For a Ti^{3+} ion substitutionally incorporated in an Al^{3+} lattice site, the degenerate $3d^1$ electron energy level is split under the influence of the local crystal field. As a result, an optical transition may occur which is vibronically broadened by strong electron-phonon coupling. Excitation to the upper level is characterised by strong absorption in the blue-green, and a radiative relaxation to the lower level gives rise to the broad fluorescence band which extends from 600nm to 1050nm. Presence of Ti^{4+} in the sapphire lattice promotes the formation of local defect structures, and is also known to interact with nearby Ti^{3+} ions, forming an additional optical absorption band[5]. These Ti^{3+}-Ti^{4+} pairs are detrimental to the lasing efficiency of bulk doped Ti:sapphire crystals, as the associated residual absorption is centred at 780nm and lies within the gain band of the $Ti^{3+}:Al_2O_3$ system.

Two diffused samples, S2 and S8, were prepared and one commercially-grown bulk-doped sample, B0, was used for comparison. The two undoped sapphire substrates were mechanically polished to optical quality with the polished face oriented perpendicular to the c-axis. Titanium oxide films 41±3nm thick were evaporated from a powdered Ti_2O_3 sourceat approximately 1nm/s, in a partial oxygen pressure of 1×10^{-4}mbar, onto both substrates. It is expected that these deposited films consist of a mixture of titanium oxides, as Ti_2O_3 is known to dissociate on heating into combinations of lower oxides[6].

Thermal diffusion was carried out in a carbon resistance furnace at a temperature of 1950°C. The annealing atmosphere is restricted to high purity argon, due to the nature of the exposed carbon heating elements. The two samples, S2 and S8, were diffused for two and eight hours respectively, defined as dwell-time at 1950°C. In both the heating and cooling phases, the diffusion couple (between sapphire and the titanium oxide source) was exposed to temporal heating gradients of 25°C/min, for temperatures in excess of 1300°C. Between room temperature and 1300°C the heating or cooling rate is significantly faster, as 1300°C is the lowest temperature at which the furnace may be controlled. Within 10 minutes of switching the furnace on or off, the temperature stabilises to 1300°C or room temperature respectively. Temporal fluctuations at the annealing temperature are typically less than ±5°C. The largest source of error is the radial heat distribution within the heating element as the estimated temperature difference between the edge and centre of the diffusion couple is 30°C. However, as sapphire has a high thermal conductivity it is expected that the diffusion temperature is uniform across the sample.

The characterisation of the diffused couples had two main objectives. First, to establish whether

the Ti has been incorporated in the appropriate lattice site and valence state to form the basis of an optical gain medium and, second, to estimate the diffusion coefficient at this temperature. These were addressed by studying the spectroscopic properties of the diffused region and subsequently by imaging the fluorescent centres onto a vidicon camera. For both these measurements, a polished section through the diffused couple was prepared in order to enhance the collection efficiency and to enable high resolution imaging of the fluorescent region.

Fluorescence originating from the near-surface region of the Ti-indiffused sapphire was excited by side-pumping a polished section through the diffused couple using light from an Ar^+ laser at 488nm. For spectral characterisation, the fluorescence was imaged onto a silicon photodetector after passing through a monochromator, as shown schematically in Figure 1. Figure 2 gives the π- and σ-polarised fluorescence spectra recorded for sample S8. The spectra extend from 600nm to 1050nm and exhibit a clear polarisation dependence. The spectra present good approximations to gaussian distributions peaking at 13200cm^{-1} (758nm) and with a FWHM intensity bandwidth of 30300cm^{-1} in the wavenumber domain, corresponding to 175nm in the wavelength domain. The measured intensity ratio of peak π-polarised to σ-polarised radiation is 0.37. These results are typical of our samples fabricated at a diffusion temperature of 1950°C, over diffusion times of up to 8 hours. The bandwidth, peak wavelength and polarisation ratio are in excellent agreement with fluorescence characteristics measured for a high quality 0.11wt% bulk doped $Ti^{3+}:Al_2O_3$ crystal (sample B0), supplied by Pi-KEM, Camberley, UK, and with published data [4].

Figure 1. Experimental configuration used to excite and collect fluorescence originating from indiffused Ti ions.

The sharp peak in the region 692-695nm, is attributed to the presence of trace amounts of Cr impurity in the sapphire substrate.

Excited-state lifetime measurements were carried out by rapidly switching the Ar^+ pump beam using an acousto-optic modulator and monitoring the fluorescence decay time. The fluorescence lifetime was measured to be $3.2 \pm 0.25\mu s$ at room temperature, which is in excellent agreement with previously published data for Ti^{3+} in sapphire at room temperature[4].

The spatial distribution of fluorescent centres at depths below the substrate surface was mapped by imaging the polished section using a vidicon camera while exciting the transition with a Ar^+ pump beam focussed to a spotsize
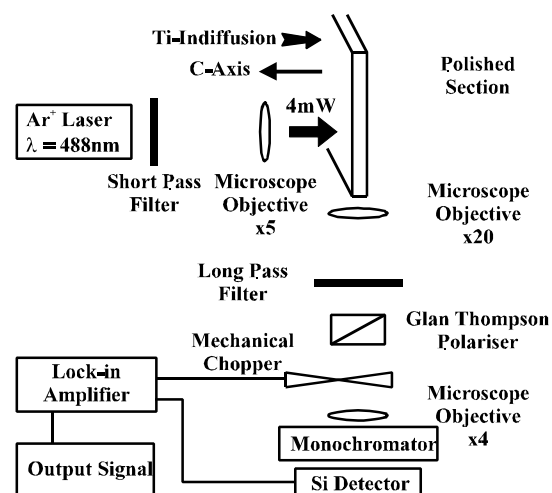

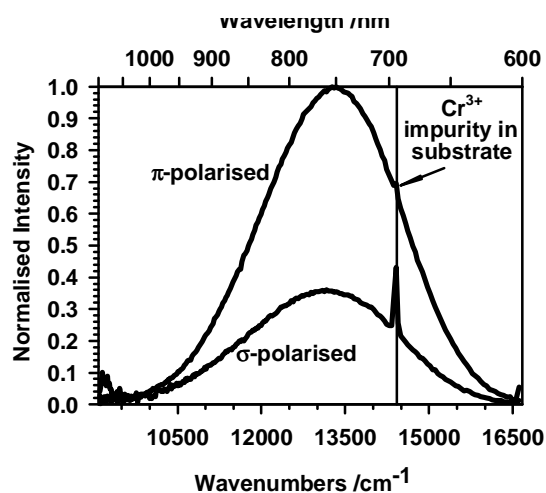**Figure 2** Polarised fluorescence spectra obtained for S8 (8 hour diffusion at 1950°C from a 41±3nm diffusion source).

of approximately 30μm diameter. The experimental configuration was similar to that illustrated in Figure 1, in terms of excitation and collection optics and sample orientation. The camera used was a Hamamatsu C1000-03 vidicon which exhibited wavelength sensitivity extending across the visible and near infra-red regime. The spatial resolution of the system was ±2μm for the magnification used. Figure 3 illustrates a central section normal to the substrate surface, through the imaged profile, for samples S2 and S8 in comparison with that obtained for the bulk-doped, commercially available Ti:Al_2O_3 sample, B0. In each case the position of the substrate surface is defined by the point of maximum gradient, and the peak has been normalised in order to aid comparison. Divergence of the pump beam and a corresponding decrease in pump power density is not significant over the region of interest, since no fall in fluorescence intensity with depth is observed for the bulk-doped sample, B0.

Prior to these measurements the depth scale was calibrated by reference to a calibrated microscope graticule.

Figure 3 shows that the measured fluorescence originates from a near-surface region of the substrate in samples S2 and S8, and is not due to a high level of Ti^{3+} impurity throughout the substrate. It is also clear that the Ti has penetrated to significant depths for both diffused samples. The data for the bulk-doped sample indicate that the resolution of the measurement is acceptable for these diffusion depths.

The accurate determination of the diffusion coefficient is complicated by the shape of the profiles, as comparison with the data for B0 shows that the peak of the fluorescence profile for the indiffused samples lies typically some 15μm below the substrate surface. Such a distribution of titanium ions is unexpected for thermal diffusion but, as the resolution of the technique has been confirmed by the measurement on the bulk-doped sample, it is believed the measurement accurately describes the distribution of fluorescent centres at the polished cross-section. These unexpected results may be interpreted by considering the fluorescence yield to be reduced at the surface where high concentrations of titanium ions may result in severe disruption of the crystal lattice or strong ion-ion interactions. Work is underway to confirm the presence of high concentrations of Ti ions in the surface region.

To obtain an estimate of the diffusion coefficient, the penetration depth was defined as the point beneath the surface at which the fluorescence intensity had fallen to 0.157 (erfc[1]) of its peak value. Samples S2 and S8 show penetration depths of 31μm and 51μm, respectively, giving a diffusion rate of order $D = 10^{-14}$ $m^2 s^{-1}$. This is several orders of magnitude greater than expected when compared with previously published lattice diffusion data for other transition metals (Cr, Fe and Ni) in sapphire[5], although faster diffusion rates have been observed for the monovalent ions silver[7] and copper[8]. The enhanced diffusion rate for Ti may be attributed to diffusion via a faster mechanism such as dislocation diffusion. Further work is currently underway to eliminate dislocation diffusion by sample pre-annealing.
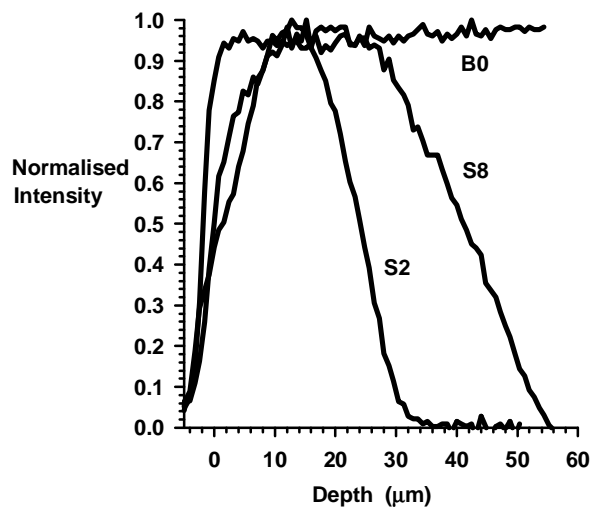

Figure 3 Ti^{3+} ion fluorescence intensity vs depth for diffused and bulk-doped Ti:sapphire samples: *S2: 2 hour diffusion, S8: 8 hour diffusion , B0: Bulk-doped sample.*

If it is assumed that all the titanium atoms diffuse into the sapphire, the penetration depth combined with the estimated Ti content in the oxide diffusion source may be used to give an order-of-magnitude estimate of the peak Ti_2O_3 concentration incorporated in the Al_2O_3 lattice. In the case of the samples described in this letter the maximum Ti concentration is estimated to be at most 0.3 wt% Ti_2O_3, which is of an order comparable to the most highly doped commercial laser crystals.

In summary, these results demonstrate that titanium may be incorporated into a sapphire lattice by thermal indiffusion. A significant proportion of the diffused Ti ions are present in a lattice site and valence state that give rise to spectroscopic characteristics in excellent agreement with those of a high quality, bulk doped $Ti^{3+}:Al_2O_3$ laser crystal. The origin of the fluorescence has been shown to be localised to the surface by imaging a polished cross-section. At a temperature of $1950^{\circ}C$, the titanium diffusion coefficient is estimated to be of the order $D = 10^{-14}m^2s^{-1}$. These results advance the development of broadband active integrated optical devices based on the local introduction of Ti^{3+} into sapphire using thermal indiffusion.

Acknowledgements

References

1.   E Lallier, D Papillon, J P Pocholle, M Papuchon, M de Micheli, D B Ostrowksy, Electron. Lett. **29**, 175 (1993)

2.   J Amin, M Hempstead, J E Román, J S Wilkinson, Opt. Lett., **19**, 141 (1994)

3.   B Lesage, A M Huntz, G Petot-Ervas, Rad. Eff. **75**, 283 (1983)

4.   P F Moulton, J. Opt. Soc. Am. B **3**, 125 (1986)

5.   R L Aggarwal, A Sanchez, M M Stuppi, R E Fahey, A J Strauss, W R Rapoport and C P Khattak, IEEE J. Quantum Electron. **24**, 1003 (1988)

6.   H K Pulker, G Paesold, E Ritter, Appl. Opt. **15**, 2986 (1976)

7.   L Badrour, E G Moya, J Bernardini, F Moya, J. Phys. Chem. Solids **50**, 561 (1989)

8.   F Moya, E G Moya, D Juve, D Treheux, C Grattepain, M Accouturier, Scripta Metall. Mater. **28**, 343 (1993)