Deep ultraviolet (UVC) laser for sterilisation and fluorescence applications

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Deep ultraviolet (UV) light can be used to sterilise bacteria and viruses, decontaminate drinking water and in fluorescence sensors to detect chemicals. We are developing a new deep UV laser technology targeting these applications. The UV laser components emit UV light in the wavelength range between 205 nm and 230 nm and we have demonstrated an output power of more than 1 mW. The laser devices offer at least ×200 increase in output power compared with LEDs emitting at the same wavelengths. We have demonstrated the use of the laser to sterilise bacteria and as the light source for fluorescence measurements.

1 Introduction

New light-emitting components which generate deep ultraviolet (UV) light will enable new markets in areas such as drinking water purification, bio-sensing and medical devices. These applications are possible because of some useful properties of ultraviolet light with wavelength between 200 nm and 280 nm – the so-called UVC band. Firstly, UVC light sterilises bacteria, viruses and fungi so it can be used in appliances for chemical-free disinfection of surfaces, air or water such as point-of-use drinking water sterilisers, air-conditioning systems and medical systems. Secondly, UVC light can initiate photocatalytic reactions which break down organic pollutants, such as pesticide residues, which are in water. This decontamination function could be used in point-of-use drinking water purifiers. A third useful property of UVC light is that it is strongly absorbed by most biological and chemical compounds and it induces fluorescence (re-emission of light with a longer wavelength) which can be characteristic of the fluorescing compound. This means that UVC light sources are very effective in fluorescence sensors to detect chemicals or bacteria in air or in water.

Exploiting these applications for UVC light requires suitable UVC-emitting components. Mercury-based UV lamps are the most common sources of UVC light. Low-pressure mercury lamps emit a narrow wavelength band centred near 254 nm and are widely used in water, air and surface sterilising systems. Although these UV lamps can generate high optical output powers of at least several watts, they do have significant disadvantages: they contain the toxic element mercury which is an environmental concern; are slow to warm up; cannot be modulated rapidly; show performance degradation at low temperatures; are fragile; require high voltages; and have lifetimes which are typically no more than 10,000 hours and are reduced by cycling.

These disadvantages of UV lamps will be overcome by development of solid-state UVC emitting devices such as LED and laser sources. There is currently a significant R&D effort to develop UVC LEDs and these are now becoming commercially available. The performance and lifetime of the devices is improving but performance at very short UVC wavelengths – less than 240 nm – remains poor. There are no low-cost and compact UVC lasers on the market – in particular there are no laser diodes which emit in this spectral range. If a UVC laser source is required for an application then the only options are expensive and bulky industrial or laboratory sources which are impractical for many applications.

At Sharp Laboratories of Europe we are developing a novel UVC laser light source which has the potential to be a mass-producible, compact and low-cost component and could be used for the applications described above. In this paper we give a review of the device and show demonstrations of some of its unique properties.

2 The diode-pumped UVC laser

Our novel UVC laser light source is based on blue/violet laser diode

technology. The device exploits a non-linear optical property possessed by certain materials known as'second harmonic generation'(SHG) or 'frequency doubling'A schematic of our device is shown in Fig. 1. The blue light output by the laser diode has a wavelength, λ, in the range 410 nm-460 nm. This blue light'pumps'a frequency-doubling component and is converted to UVC light with wavelength λ/2 which is in the range 205 nm-230 nm. The frequency-doubling process, which is the same as'wavelength-halving'can be thought of as pairs of blue photons combining to form single UVC photons. The emitted light has the features characteristic of a UVC laser. In particular, the output can be modulated at high speed and the emitted UVC light is monochromatic, coherent, linearly polarised and can be collimated into a beam or focused to a small spot. We call it the diode-pumped UVC laser (dpUVC-laser).

One of the biggest challenges in developing the dpUVC-laser is to achieve good efficiency in the frequency-doubling component. The choice of frequency-doubling material is limited because the majority of common non-linear optical materials absorb deep UV light. Furthermore, to meet the critical condition for efficient SHG (known as phasematching) at the wavelengths we desire we also need a highly birefringent material. The most suitable non-linear optical material to use is β-BaB_2O_4 which is commonly known as BBO.

BBO does not naturally offer efficient frequency-doubling of light from blue laser diodes because it has a relatively small second order non-linear optical coefficient. We are developing several methods to increase the efficiency of the frequency-doubling in BBO and thereby increase the efficiency and output power of the dpUVC-laser.

One very effective method is to fabricate an optical waveguide which confines the blue and UVC light into a small cross-sectional area as they pass through the BBO. The waveguide is effective because the frequency-doubling efficiency depends on the intensity of the light within the BBO (intensity = power ÷ cross-sectional area). Decreasing the cross-sectional area of the light by confining it in a waveguide increases the intensity and increases the frequency-doubling efficiency. We have developed a novel method to create thin films of BBO single crystal with thickness in the range of 5-20 μm which act as planar waveguides and significantly increase the frequency-doubling efficiency. We also modify these thin films to form two-dimensional waveguides which provide further confinement of the propagating light into even smaller areas. A challenge for these methods is that BBO is hygroscopic – it absorbs moisture – and water absorption leads to BBO becoming an absorber of deep UV radiation which extinguishes all UV emission. Therefore, we have developed all of our material handling processes so that they can be carried out without the use of water or any water-containing chemicals. In the device we cover the material in a protective coating and/or encapsulate it in a dry atmosphere and this provides stable operation over long lifetimes.

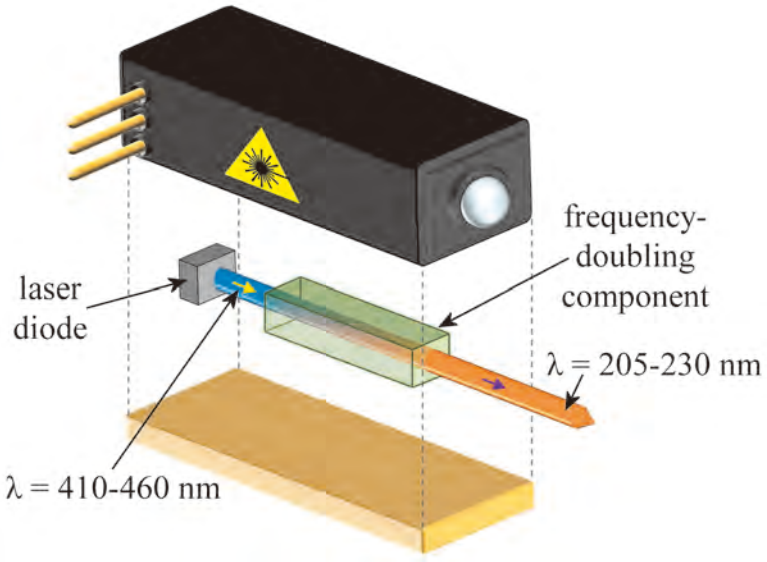

Fig. 1 A schematic diagram of the diode-pumped UVC laser.

There are several key challenges relating to the integration of the laser diode with the frequency-doubling component. One important design consideration is to ensure that the light emitted by the laser diode has a sufficiently narrow spectral linewidth and stable wavelength to remain matched with the wavelength acceptance range of the frequency-doubling component. A second important feature is to increase the overall UVC output power by filtering and re-using the blue light which passes through a frequency-doubling component without being converted to UVC.

Our frequency-doubling components can be adapted to generate UVC with wavelength from 205 nm to more

than 280 nm (i.e. laser diode emission wavelengths between 410 nm and at least 560 nm). At the moment the highest performance laser diodes emit wavelengths between 410 nm and 460 nm so we are focusing on dpUVC-laser devices with UVC wavelengths between 205 nm and 230 nm.

3 Device properties

We have fabricated dpUVC-laser devices emitting at several wavelengths in the range from 207 nm to 223 nm. The UVC spectra for four of our devices are shown in Fig. 2. The output from each device is essentially monochromatic with a wavelength full-width half-maximum (FWHM) of less than 1 nm. Our highest power device has a wavelength of 222 nm and output power of 1.1 mW (pulsed operation).

Two advantages of the dpUVC-laser over the emerging technology of UVC LEDs are the very short operating wavelength of less than 230 nm and the laser-like nature of the emitted light. The plot in Fig. 3 shows a comparison of the wavelength and output powers reported for R&D UVC LEDs (blue triangles) [1-7] and those of our dpUVC-lasers (red square is continuous operation(cw); red circle is pulsed operation; red lines are projected power for devices with laser diodes emitting shorter wavelengths). The plot shows that for wavelengths of between 205 nm and 230 nm the UV laser power is between ×200 higher and ×2000 higher than the best reported R&D LEDs. We are not aware of any commercially available LEDs emitting in this 205 nm-230 nm wavelength range. The laser-like beam properties of the dpUVC-laser mean that the UVC beam can be collimated or focused into a much smaller area than is possible with large-area light sources such as mercury lamps or LEDs. For example, we have focused the full power of a dpUVC-laser into an area of ~10 µm × 10 µm using a single lens. The ready focusability means that the UV light can be efficiently coupled into optical fibres so that the action of the UV light may be spatially remote from the UV source. Also, the UV light can be provided with very high power densities: we have already demonstrated focused spots with power densities of at least 400 mW·cm^{-2} (222 nm wavelength) and we expect values of up to several W·cm^{-2} are achievable. High power densities are attractive for fluorescence excitation applications or very rapid sterilisation of small volumes or surfaces. If an application requires UVC light over a large area then the light emitted from the UVC laser can be spread into a broad beam using simple optics.

4 Sterilisation using the UVC laser

We have carried out surface-sterilisation tests to demonstrate the sterilising effect of the dpUVC-laser. Bacteria were seeded onto the surface of an agar plate and then the UVC laser beam was rastered over the infected surface to sterilise the bacteria in predetermined regions. The dpUVC-laser beam with wavelength 222 nm was loosely focused with a lens to form a spot size of approximately 0.5 mm × 0.5 mm and an energy density of 10 mJ·cm^{-2} was delivered to each "pixel" (this would take 0.025 seconds with a 1 mW beam). This dose of UVC

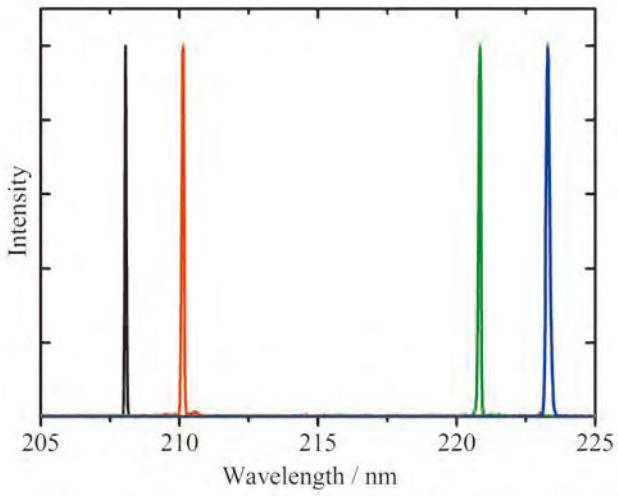

Fig. 2 Output spectra from four different dpUVC-laser devices.

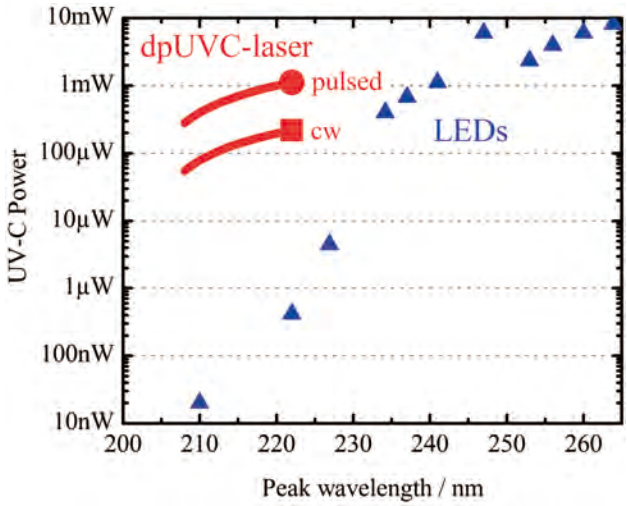

Fig. 3 A comparison of the output wavelength and power of R&D UVC LEDs reported in the literature (blue triangles) and the SLE dpUVC-laser (red square, circle and lines).

light is sufficient to achieve between 99.9% to 99.99% deactivation of bacteria on a surface. For this edition of the SHARP Technical Journal, which falls in SHARP Corporation's centenary year, we used the UVC light to sterilise a "SHARP 100" pattern on the infected surface.

A photograph of the agar plate after incubation for 24 hours at 37℃ is shown in Fig. 4. Where the agar surface was irradiated by the UVC laser the seeded bacteria were irreparably damaged and were unable to reproduce. The agar surface remains a dark brown colour which indicates no bacteria reproduction and demonstrates the effective sterilisation of the bacteria. Elsewhere the seeded bacteria could reproduce as normal and they multiplied during the incubation period to form colonies which are visible as pale spots in the photograph.

The clear definition of the "Sharp 100" logo in Fig. 4 demonstrates the sterilising effect of the UVC laser. Importantly, it also demonstrates that the UVC laser output beam can be very easily and effectively focused into a small spot size and delivered from a long distance away. The sterilisation occurred only within the intended area of the spot size and the surface immediately adjacent was unaffected, even though the UVC laser device was at least 300 mm away from the agar plate (we stress that the pattern in Fig. 4 is obtained without any masking of the surface, and simply by rastering of the UVC beam). This function may enable new applications using UVC-based sterilisation. As well as this, the very short wavelength of our device (less than 230 nm) may show good potential for sterilisation of bacteria and viruses which are resistant to longer-wavelength UVC light.

5 Fluorescence using the UVC laser

We have also demonstrated the potential of the dpUVC-laser for use as a light source for fluorescence bio- or chemical-sensors which could be used to detect chemical or biological molecules or bacteria. In fluorescence measurements, photons of the excitation light are absorbed by a specimen and fluorescent photons with lower energy (longer wavelength) are emitted. Analysis of the fluorescent light can be used in a sensor to detect the presence and/or quantity of a particular chemical or biological molecule. An excitation source must be strongly absorbed by the target molecule and must have photon energy higher than the fluorescent photon energy. The very deep ultraviolet light generated by the dpUVC-laser (wavelength less than 230 nm) is excellent in both of these respects: it is very strongly absorbed by many organic chemicals, including some amino acids in proteins, and has very high energy which enables many fluorescence processes. It is often advantageous for the excitation light used in a fluorescence measurement to be monochromatic and to be focused into a small spot. This means that the laser-like beam emitted by our device is very well suited to this application.

The plots in Fig. 5 show the fluorescence spectra measured when the dpUVC-laser was used to pump an aqueous solution of naphthalene (top) and a surface coating of the bovine serum albumin (BSA) protein (bottom). We use naphthalene to illustrate the potential for chemical-sensors and BSA to illustrate the potential for use in bio-sensors. In each case the UVC laser is visible as a sharp peak at a wavelength of approximately 220 nm and the fluorescence is a broader peak in the 280 nm-400 nm range (note that the

Fig. 4 A demonstration of sterilisation of bacteria using the dpUVC-laser. The dpUVC-laser beam was rastered to sterilise the surface in the pattern of a "SHARP 100" logo. The pale spots are bacterial growth; the dark brown area of the logo was sterilised. The diagram on the right shows the sterilisation setup.

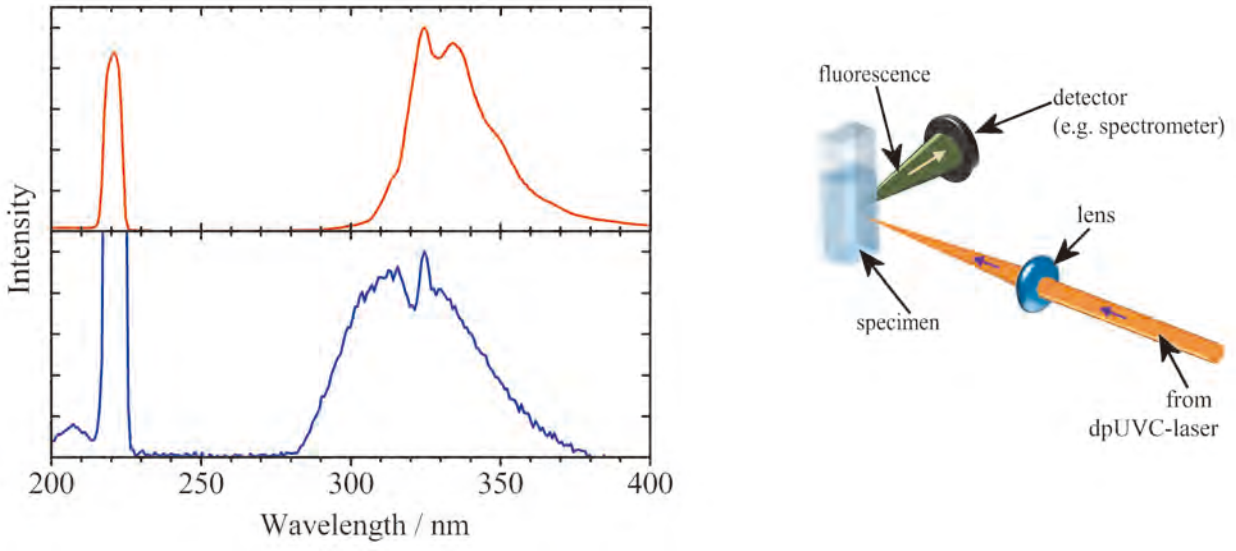

Fig. 5 Plots of fluorescence spectra from naphthalene (top) and BSA protein (bottom) after excitation with the dpUVC-laser. The diagram on the right shows a typical fluorescence setup.

spectral width of the laser emission is overestimated due to the low-resolution of the spectrometer used for this measurement). These results show the strong potential of the dpUVC-laser as a fluorescence excitation source.

6 Conclusion and future plans

We have demonstrated a UVC laser device with output power of more than 1 mW. Our device is all-solid-state and can generate light in the important wavelength range between 205 nm and at least 230 nm. The output power is more than ×200 higher than the output from LEDs at the same wavelengths.

The mW-class output power is high enough for the device to be used in some applications, in particular for fluorescence excitation and for some sterilisation applications. We are now working to reduce the size of the mW-class device into a compact component and one which can operate in continuous wave (cw) mode. In addition, we are carrying out several developments to achieve large increases in the efficiency of the frequency-doubling component so that the UVC output power can be increased to 10 mW and above. This increased output power will open up new applications for the device.

We will also continue to investigate new applications which benefit from the unique properties of the device such as the monochromatic and short UVC emission wavelength and the ability to focus the UV light into small spots with very high power density.

References

1) Taniyasu et al., Nature **441** p325 (2006)
2) Noguchi et al., physica status solidi (c) **6** S459 (2009)
3) Hirayama et al., Applied Physics Express **1** 051101 (2008)
4) Hirayama et al., physica status solidi (a) **206** 1176 (2009)
5) Shatalov et al., Applied Physics Express **3** 062101 (2010)
6) Grandusky et al., Applied Physics Express **4** 082101 (2011)
7) We have calculated the average output power where published data were only provided for pulsed testing conditions.