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https://en.wikipedia.org/wiki/Raman_Laser

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INT CL **C01B, C23C, C30B, H01S**
Other: **WPI, EPODOC, Patent Fulltext**

(54) Title of the Invention: **Raman laser system**
Abstract Title: **Raman Laser System**

(57) A diamond Raman laser system comprising a laser for providing laser light having a wavelength less than 750 nm, the laser comprising at least one pump laser and further comprising a Raman oscillator, the at least one pump laser and the Raman oscillator being configured to provide an n-order Raman oscillation, where n is an integer. The Raman oscillator comprises single crystal diamond, the single crystal diamond having an optical absorption coefficient measured by optical spectroscopy at 450 nm of less than 0.5 cm-1.

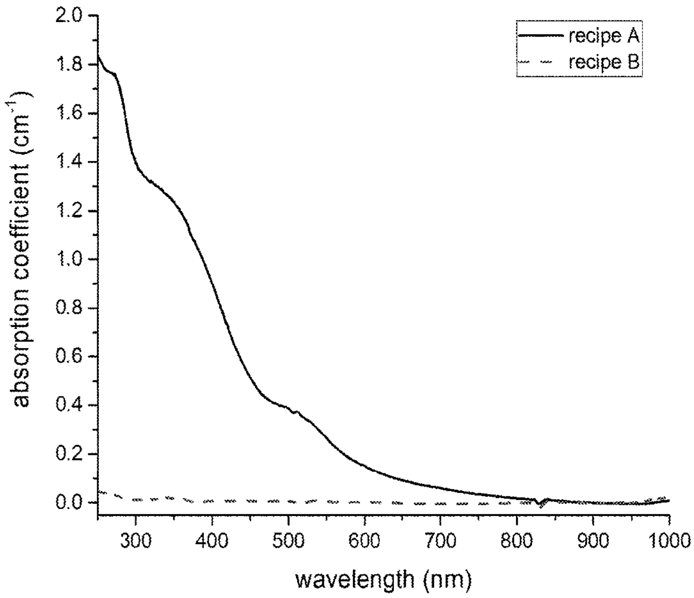

Figure 4

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

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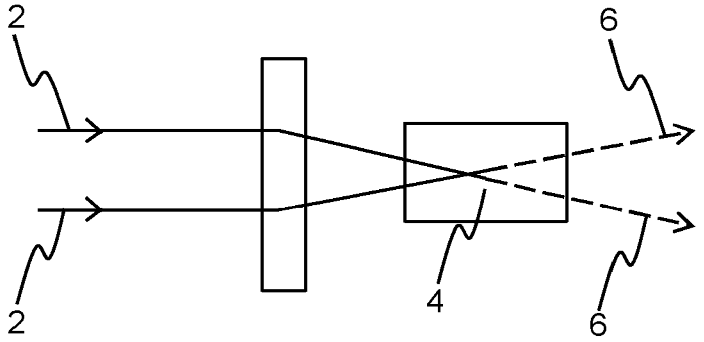

Figure 1

23 11 22

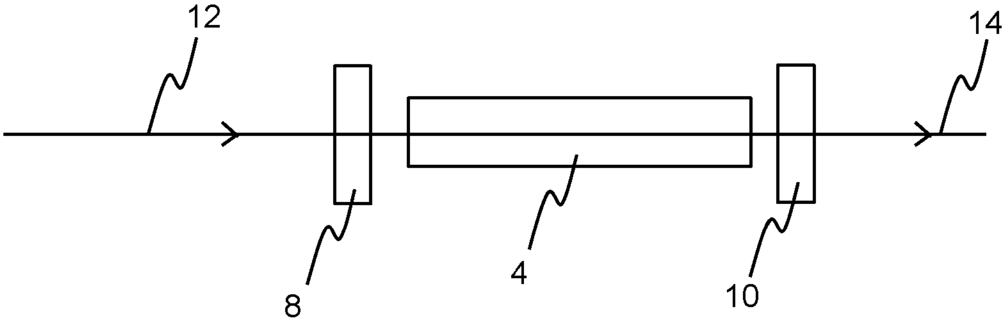

Figure 2

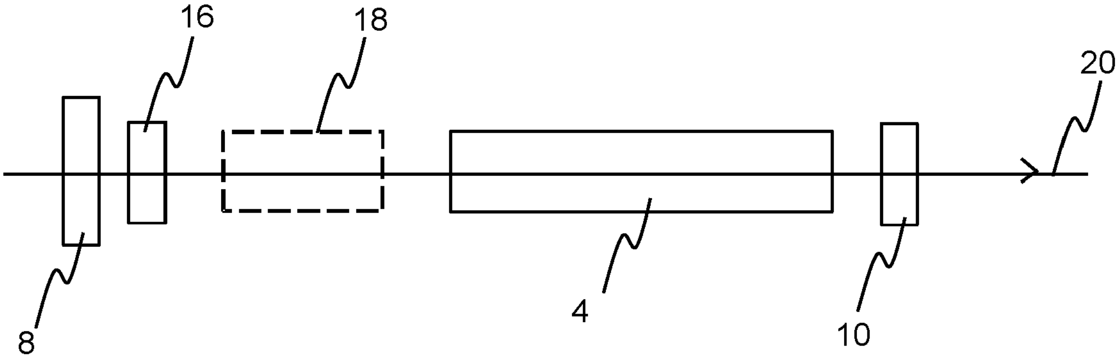

Figure 3

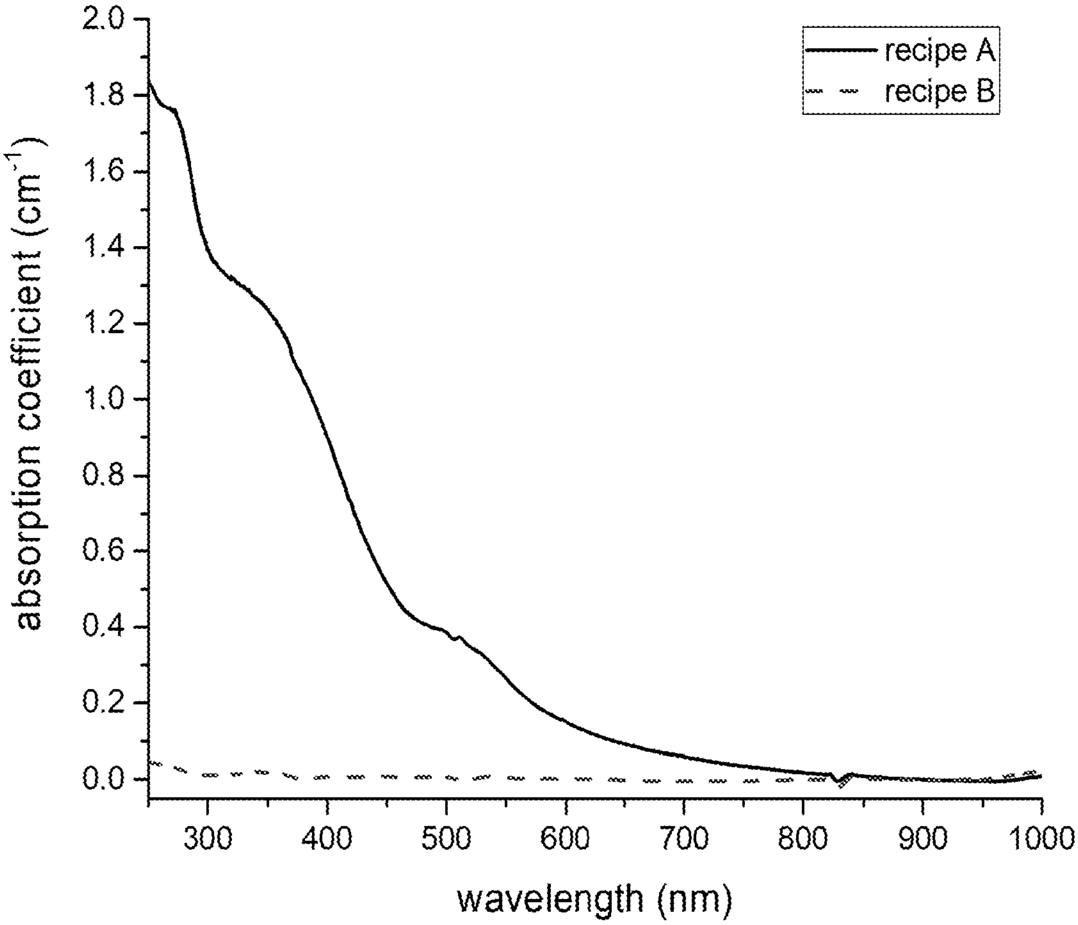
recipe A
recipe B
absorption coefficient (cm^{-1})
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
700
800
900
1000
wavelength (nm)

Figure 4

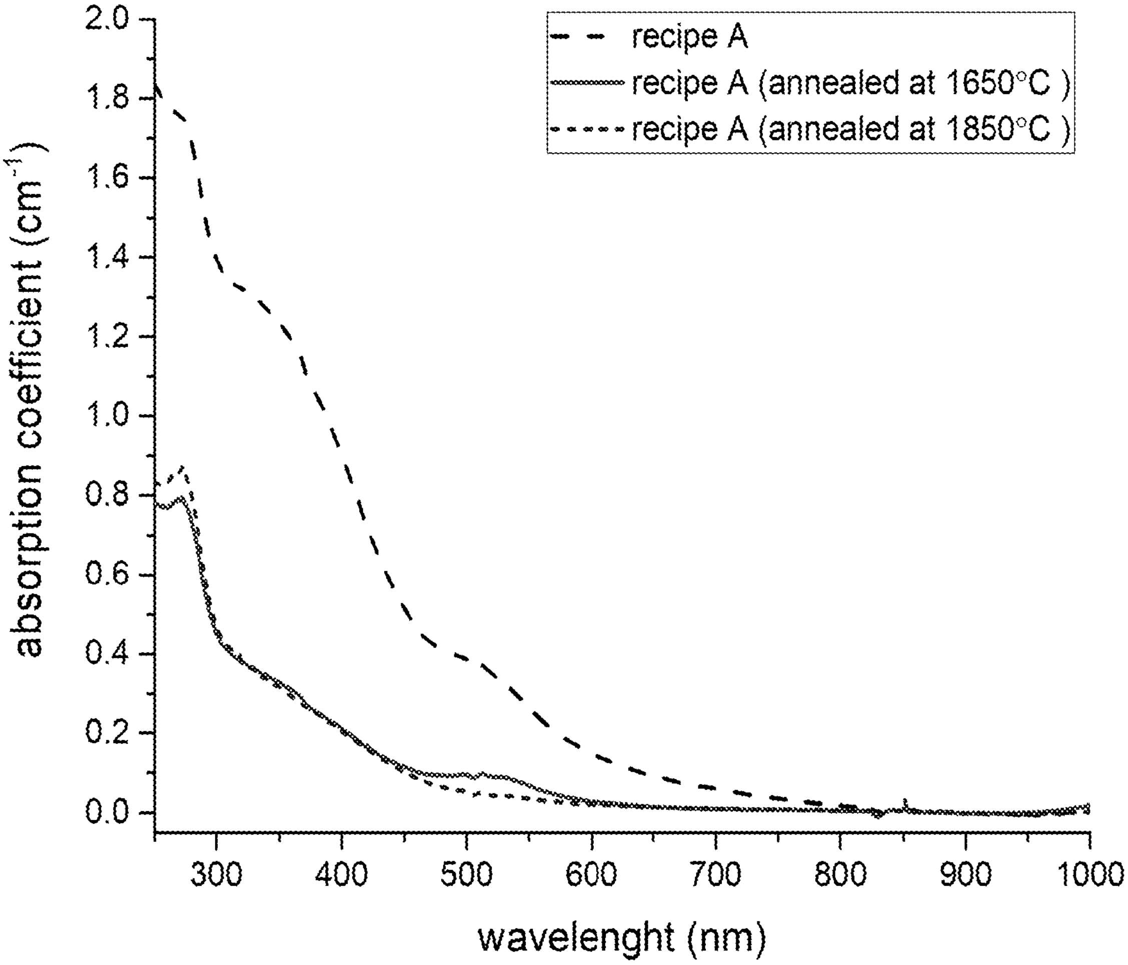
absorption coefficient (cm^{-1})
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
700
800
900
1000
wavelenght (nm)
recipe A
recipe A (annealed at 1650°C)
recipe A (annealed at 1850°C)

Figure 5

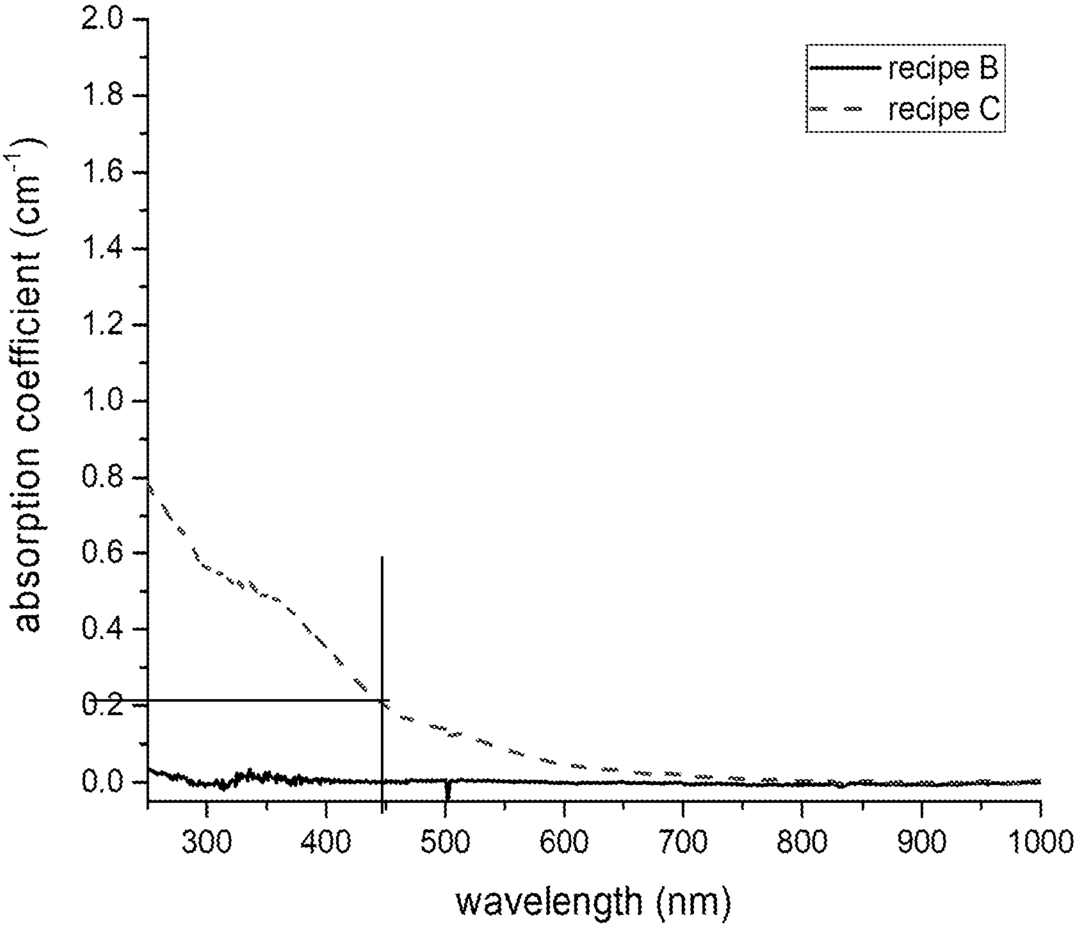
absorption coefficient (cm^{-1})
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
700
800
900
1000
wavelength (nm)
recipe B
recipe C

Figure 6

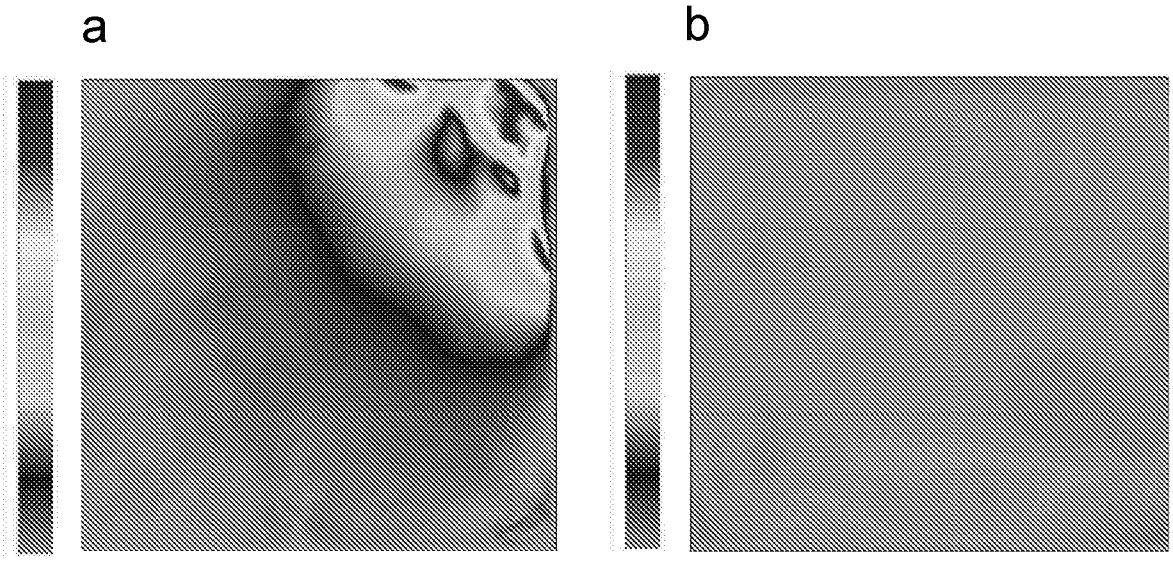

Figure 7

RAMAN LASER SYSTEM

FIELD OF THE INVENTION

This invention relates to Raman laser systems, and particular Raman laser systems that use diamond.

BACKGROUND

Chemical vapour deposition (CVD) is an established technique for depositing material onto a substrate. The technique has been extensively described in patent and other literature. For deposition of diamond, the CVD process typically involves providing a gas mixture that, on dissociation, can provide carbon and hydrogen. The dissociation of the source gas mixture is brought about by an energy source, such as microwaves, radio frequency energy, a flame, a hot filament or jet-based technique. The reactive species are allowed to deposit onto a suitable substrate, typically held at between 700°C and 1200°C, to form diamond.

The minimisation of the presence of defects within CVD diamond is of utmost importance for several applications. There are different types of defects that occur in CVD diamond. Point defects can occur when impurities in the growth atmosphere are incorporated into the diamond lattice. Another type of defect is a dislocation. Dislocations form within the crystal, possibly due to the formation of pits on the diamond growth surface, and can further multiply during growth. Such pits may also be responsible for the inclusion of other defects and impurities.

The increasing presence of these defects is detrimental to several properties of the CVD diamond material. An increasing presence of all types of defects affects certain properties, for example, decreasing the thermal conductivity (as phonons are scattered). The point defects also affect absorption of photons and are therefore deleterious to optical transparency. Dislocations result in local birefringence due to their anisotropic disruption of the cubic symmetry of the lattice and so are also detrimental to the optical properties of the diamond material.

It has been found that dislocations in homoepitaxial CVD diamond layers tend to nucleate at or near the interface with their substrate. It has also been found that dislocations generally have line directions that are close to perpendicular to the local growth surface and that, as a result, the strain-related birefringence shows a characteristic anisotropy, being much more obvious for a viewing direction parallel to the growth direction.

WO2004/046427 describes the production of diamond material via the CVD process by utilising a controlled, low level of nitrogen to control the development of the crystal defects. It is described how nitrogen present in the CVD diamond material must be sufficient to prevent or reduce local strain generating defects whilst being low enough to prevent or reduce deleterious absorptions and crystal quality degradation.

Single crystal diamond finds a potential application within Raman lasers, as described in US2005/0163169. Such an application places severe requirements on the diamond material that can be utilised.

Raman lasers rely on the process of Raman scattering. Spontaneous Raman scattering occurs when a photon incident on a material results in the excitation of a vibrational mode from its initial energy level to an excited, virtual state. This virtual state can then return to an energy level different to the original level, producing a photon of different energy (and frequency) to that of the incident photon. For the majority of the spontaneously Raman scattered photons the final energy level is higher than the initial level, the scattered photon therefore has a lower energy than the incident photon, this is termed Stokes scattering. The energy difference between the incident and scattered photons results in the production of a phonon (a quantised lattice vibration).

In a Raman laser the scattered photon is utilised to stimulate further Raman scattered photons of the same wavelength: stimulated Raman scattering (SRS). This is achieved by feeding the scattered photon back into the Raman scattering medium, commonly by keeping the Raman scattering medium within an appropriate optical resonator, as described in Optics Express, 2008 **16** (23), pages 18950-18955 and Optics Letters, 2009 **34**, pages 2811-2813.

In spontaneous Raman scattering it is also possible to observe second Stokes photons due to the Raman scattering of the first Stokes photon. This process can be repeated further such that a succession of higher order Stokes photons are observed with frequencies equal to the pump photon frequency minus an integer number of the characteristic phonon frequency. In a Raman laser, these higher order Stokes wavelengths can in principle be engineered to be the main emission wavelength of the device by simply designing the optical cavity to resonate at the desired Stokes wavelength.

The Raman laser is therefore capable of changing the frequency of the input light, advantageously producing an output beam with a frequency in a part of the electromagnetic spectrum that was previously unattainable with conventional laser technology.

Single crystal diamond is a promising material for use as the Raman scattering medium within the Raman laser. It has a high Raman gain coefficient, possesses low absorbance in a wide range of the electromagnetic spectrum (allowing versatility in the choice of input, intermediate and output frequencies), it is a good dissipater of thermal energy which is generated in the form of phonons as an integral part of the process, and possesses a low thermal expansion coefficient (minimising temperature related distortions).

The Raman gain coefficient, g_R, is defined as

$$g_R = const \times \frac{T_2}{\lambda_S} \qquad \text{(Equation 1)}$$

where T_2 is the optical phonon decoherence time, λ_s is the Stokes-shifted output wavelength and *const* is a material dependent constant of proportionality.

The polarisation of the pump beam with respect to the symmetry axes of the crystal is a parameter which affects the Raman gain coefficient. For a linearly polarised pump beam with polarisation vector along a <110> direction, the Stokes beam is polarised parallel to the pump beam. For a pump beam polarised along a <100> direction the Stokes beam is polarised perpendicular to the pump beam. This suggests a particularly convenient crystallographic configuration of the diamond gain crystal, in which a rectangular block with two pairs of {110} faces and one pair of {100} faces is manufactured. By pumping the diamond Raman scattering medium crystal through a {110} face at the Brewster angle with *p*-polarised light, reflections at the incident and exit faces are eliminated for both the pump and Stokes beams. An even better configuration entails processing Brewster facets on the incident/exit faces, such that the pump beam within the crystal proceeds along the <110> direction. This then ensures that there is no component of the pump beam direction perpendicular to the length of the cavity and so there is also no risk of the pump beam exiting one side of the crystal and that the pump beam lies accurately on the <110> direction.

By engineering the diamond in such a way as to accommodate Brewster angle pumping, the requirement for anti-reflection coatings, which add cost and complication, is avoided.

Diamond Raman lasers can operate in a number of configurations. The most simple is as a Raman generator, as illustrated in Figure 1, in which a high intensity pulsed pump laser 2 is focused onto the diamond Raman gain crystal 4, resulting in conversion of the pump wavelength to multiple Stokes orders which constitute the output beam 6 of the laser. Although this is a relatively simple design which does not require an optical cavity, in practice such a configuration is of little use due to the limited control of the output spectrum

A second type of configuration is as an external Raman resonator, as illustrated in Figure 2. Here the Raman crystal 4 is placed within an optical resonator comprising an input mirror 8 and an output mirror 10 in order to reduce the SRS threshold, increase the conversion efficiency and tailor the output wavelength 14. In this configuration the cavity is pumped externally with either a continuous wave (cw) or pulsed laser source 12. Due to diamond's high Raman gain coefficient the Raman crystal can be kept short compared to other Raman gain materials. Such an external diamond Raman resonator can therefore be viewed as a simple, compact add-on enabling frequency conversion for a wide variety of laser sources.

A third configuration is an intracavity Raman resonator, as illustrated in Figure 3, in which both the pump laser medium 16 and the Raman crystal 4 are placed within a cavity, comprising input mirror 8 and output mirror 10, resonant at both pump and Stokes wavelengths. This configuration takes advantage of the high intracavity pump field which leads to enhanced conversion to the output beam 20. The cavity may also include other optical elements such as a Q-switch 18 for pulsed mode operation.

SUMMARY OF THE INVENTION

There is a requirement for high power, short wavelength lasers with a good beam quality. These may be used in a number of industrial applications, such as cutting, welding and soldering of high reflectance metals. Raman lasers may be used for such applications. However, at wavelengths in the shorter wavelength region of the UV-visible range (e.g. 300-500nm), several defects in diamond such as single substitutional nitrogen in the neutral charge state, N_s^0, vacancy clusters and other defects comprising some or all of nitrogen, lattice vacancies and hydrogen, such as NVH^0, can increase the optical absorption. The presence of these defects typically leads to a general increase in the absorption coefficient with decreasing wavelength. This in turn leads to enhanced optical losses in Raman lasers operating at shorter wavelengths in the UV-visible range, giving a loss of efficiency and an increase in the Raman laser pumping threshold.

By minimising dislocations within the diamond, the birefringence can be minimised, which minimises depolarisation losses in diamond Raman laser systems in which the polarisation is a controlled design parameter.

It is an object to provide a Raman laser system using diamond that addresses these problems.

According to a first aspect of the invention, there is provided a diamond Raman laser system. The system comprises a laser for providing laser light having a wavelength less than 750 nm, the laser comprising at least one pump laser and further comprising a Raman oscillator, the at least one pump laser and the Raman oscillator being configured to provide an n-order Raman oscillation, where n is an integer. The Raman oscillator comprises single crystal diamond, the single crystal diamond having an optical absorption coefficient measured by optical spectroscopy at 450 nm of less than 0.5 $cm^{-1.}$

As an option, the single crystal diamond has an average optical birefringence, measured at 20°C along the direction of pump or Stokes beam propagation, such that the birefringence over at least 80% of the cross-sectional area does not exceed 2×10^{-5}.

The single crystal diamond optionally has an optical absorption measured by optical spectroscopy at 450 nm selected from any of less than 0.3 cm^{-1}, less than 0.2 cm^{-1} and less than 0.1 cm^{-1}.

As an option, the single crystal diamond comprises a single substitutional nitrogen, N_s^0, concentration as measured by electron paramagnetic resonance, EPR, selected from any of less than 100 ppb, and less than 50 ppb.

The single crystal diamond optionally comprises a single substitutional nitrogen, N_s^0, concentration as measured by electron paramagnetic resonance, EPR, selected from any of greater than 5 ppm and greater than 10 ppb.

As an option, the diamond Raman laser system has an operating power selected from any of at least 200 W, at least 500 W, at least 1000 W, and at least 1500 W.

As an option, the diamond Raman laser system has a beam parameter product selected from any of less than 60 mm·mrad, less than 40 mm·mrad, less than 20 mm·mrad, less than 10 mm·mrad, and less than 5 mm·mrad.

The laser optionally has a Stokes wavelength in a range selected from any of 240 to 700 nm, 300 to 600 nm and 400 to 500 nm.

As an option, the pump laser comprises at least one laser diode. As a further option, the pump laser comprises a plurality of laser diodes. As a further option, the plurality of laser diodes are coupled together by optical fibre.

The single crystal diamond is selected from any one of chemical vapour deposition, CVD, diamond, high pressure high temperature, HPHT, diamond, and natural diamond.

As an option, the single crystal diamond has an anti-reflective surface coating.

As an option, the single crystal diamond has been annealed at a temperature of at least 1400°C to reduce the absorption coefficient.

The diamond Raman laser system optionally comprises a heat sink in thermal contact with the single crystal diamond.

The single crystal diamond optionally forms a first layer in a composite single crystal diamond, the composite single crystal diamond further comprising a second layer of single crystal diamond, the second layer having a higher single substitutional nitrogen concentration than the first layer. The second layer may therefore form an integral heat sink. The composite single crystal diamond may comprise a third layer of single crystal diamond embedded in the heat sink.

As an option, the diamond has a linear dimension in the path of the laser of at least 2 mm.

According to a second aspect, there is provided use of a diamond Raman laser system as described above in the first aspect.

As an option, the diamond Raman laser system is used for processing materials having a low infra-red absorption. Examples of such materials include copper and platinum. Examples of a use include machining or welding.

BRIEF DESCIPTION OF THE DRAWINGS

The invention will now be more particularly described, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 illustrates schematically in a block diagram a Raman laser in a known Raman generator configuration;

Figure 2 illustrates schematically in a block diagram a Raman laser in a known external Raman resonator configuration;

Figure 3 illustrates schematically in a block diagram a Raman laser in a known intracavity Raman resonator configuration;

Figure 4 shows the optical absorption spectra of examples diamonds made using recipes A and B;

Figure 5 shows the optical absorption spectra of examples diamonds made using recipes A using different heat treatments;

Figure 6 shows the optical absorption spectra of examples diamonds made using recipes B and C; and

Figure 7 shows birefringence for an exemplary CVD single crystal diamond.

Throughout the description, similar parts have been assigned the same reference numerals, and a detailed description is omitted for brevity.

DETAILED DESCTIPION

The use of diamonds in Raman laser systems has been described above. However, recent developments in Raman laser systems include Raman laser systems that use shorter wavelengths of less than 750 nm. Such systems are being developed and are described, for example, in US2020/0180080. However, a problem with diamond is that the optical absorption is not uniform across the optical spectrum, and diamond that may be suitable at wavelengths greater than 1064 nm may not be suitable for shorter wavelengths. If one were to substitute diamond from a higher wavelength Raman laser system into a lower wavelength Raman laser system, one may be surprised to find that the diamond does not perform as well in the lower wavelength Raman laser system. It is a requirement that the absorption of the diamond is as low as possible at the operating wavelength, but it has been found that at wavelengths of, for example, 450 nm, certain defects in diamond that are not detrimental at higher wavelengths give rise to higher absorption at shorter wavelengths. Examples of such defects include vacancy clusters which do not significantly impact the absorption at 1064 nm, but have a significant effect on the absorption at 450 nm.

The inventors have found that diamond can be optimised for use in Raman laser systems operating at wavelengths below 750 nm, for example at 450 nm, by careful control of defects that would otherwise introduce significant absorption at 450 nm. In practice this can be done through control of the synthesis conditions, control of post-synthesis treatment such as annealing, or a combination of both.

Examples

The following examples show how the absorption coefficient of single crystal diamond at 450 nm can be controlled by synthesis conditions and by post-growth annealing. Absorption spectra are shown to illustrate how significant these changes are at 450 nm compared to at ~1 µm where the absorption coefficient for the same diamond changes by much smaller amounts.

In all examples, single crystal CVD diamond was grown in a microwave plasma reactor comprising a temperature monitoring system and substrate temperature control system. The microwave plasma reactor comprises the following basic components: a plasma chamber; a substrate holder; a microwave generator for forming a plasma within the plasma chamber; a microwave coupling configuration for feeding microwaves from the microwave generator into the plasma chamber via dielectric windows; and a gas flow system comprising source gases, one or more gas inlets, and one or more gas outlets for feeding process gases into the plasma chamber and removing them therefrom. Such a system is described in WO2013/087697.

The plasma chamber is configured to form a resonance cavity supporting a standing microwave in use. According to one configuration the plasma chamber is configured to support a TM_{01n} standing microwave in use, e.g. a TM_{011} mode. The operational frequency may be in a range 400 to 500 MHz, 800 to 1000 MHz, or 2300 to 2600 MHz. Source gases including a carbon source and molecular hydrogen are fed into the plasma reactor vessel and can be activated by the standing microwave field to form a plasma in high electric field regions. A substrate configuration is provided in close proximity to the plasma such that reactive carbon containing radicals can diffuse from the plasma to the substrate and be deposited thereon. Atomic hydrogen can also diffuse from the plasma to the substrate and selectively etch off non-diamond carbon from the substrate such that diamond growth can occur.

The microwave plasma reactor further comprises one or more temperature measurement devices configured to take at least two temperature measurements, including one or more measurements in a central region of the support substrate and one or more measurements in a peripheral region of the support substrate. The temperature measurements may be taken simultaneously or within a short time interval of each other and the substrate temperature control system may be used to correct any temperature variations. The temperature measurement device may comprise a pyrometer. Two pyrometers may be provided, one to take the central temperature measurements and one to take the peripheral temperature measurements. Alternatively, a plurality of thermocouples can be embedded into the substrate. Pyrometric measurements may focus on the temperature of the growing CVD synthetic diamond material. However, as the material is in good thermal contact with the underlying support substrate then the temperature of the diamond material will be approximately the same as the temperature of the underlying support substrate. For single crystal CVD synthetic diamond growth in which a plurality of single crystal diamond substrates are provided on the support substrate, the temperature measurements may thus be taken between the growing CVD single crystals.

Even when utilizing arrangements such as those described above, a number of problems may still exist, although these may be substantially alleviated by the previously described arrangements. For example, in some instances there may still be issues of non-uniform CVD synthetic diamond growth and non-uniform uptake of nitrogen across the support substrate area, particularly when growing a plurality of single crystal diamond crystals in a single growth run on a plurality of single crystal diamond substrates adhered to a support substrate over a relatively large area (e.g. 80 mm diameter or more). This is particularly problematic as there is an ongoing need to increase the area over which uniform CVD synthetic diamond can be grown. Furthermore, these problems tend to be exacerbated when the support substrates are reused in subsequent growth runs. This is particularly problematic for refractory metal substrates which are expensive and reuse is desirable in an economically competitive industrial process.

Table 1 shows three exemplary recipes for CVD diamond growth using the system described above.

Table 1

Recipe	**Power density (Wmm^{-2})**	**Pressure (T)**	**CH_4:H_2 (%)**	**N_2 (ppm)**	**Temperature (°C)**
A	1.9	185	6	0.7	880
B	1.9	185	5	0.08	860
C	1.9	185	5	0.08	800

Recipe A contained significantly more gas-phase nitrogen than recipes B and C and was prepared at a higher temperature. It can therefore be expected that the concentration of nitrogen and other absorbing optical defect centres in the diamond of recipe A would be significantly higher than that of recipes B and C. The estimated concentrations of Ns0 are 150 ppb for recipe A, and 20 ppb for recipes B and C, within ± 30%.

Once the samples were prepared, they were cleaned to remove any polycrystalline diamond, and cut and polished to form plates with a largest linear dimension of around 4 mm and a thickness of around 1 mm. Cutting and polishing to form parallel plates was required in order to produce samples that gave reproducible optical absorption spectra.

Optical absorption was measured by UV-vis spectroscopy, as is well known in the art. Simply, a beam of radiation at the desired wavelengths is directed through a sample, and the intensity of the radiation that is transmitted through the sample is measured. The intensity of the transmitted radiation can be used to calculate the absorption coefficient. Note that optical absorption may also be measured using calorimetry, which is a more sensitive technique than UV-vis spectroscopy.

Figure 4 shows the optical absorption spectra of recipes A and B. It can be seen that both Recipe A and Recipe B have a low absorption coefficient at a wavelength of around 1 μm and, accordingly, both types of diamond would be suitable for use in a diamond Raman laser system operating at a wavelength of, say, 1064 nm. However, at 450 nm, the absorption coefficient of Recipe B remains low at less than around 0.05 cm^{-1}, (the measured value was 0.007 cm^{-1})whereas the absorption coefficient of Recipe A at 450 nm is much higher, between 0.5 and 0.6 cm^{-1} (the measured value was 0.515 cm^{-1}) This means that Recipe A, while suitable for use in a diamond Raman laser system operating at 1064 nm, would not be suitable for use in a diamond Raman laser system operating at 450 nm, as the higher absorption would lead to unacceptable optical losses, which can lead to a higher Raman lasing threshold and lower optical efficiency.

The careful control of absorbing defects such as those containing nitrogen, and vacancy clusters, has been shown to allow the absorption properties of diamond to be optimised for use in a diamond Raman laser system operating at wavelengths below 750 nm.

In a further experiment, diamond made using Recipe A was annealed at temperatures of 1650°C and 1850°C under diamond-stabilizing pressure. Figure 5 shows the UV-vis absorption spectra of Recipe A without annealing, annealed at 1650°C and annealed at 1850°C.

It can be seen that annealing greatly reduced the absorption coefficient at 450 nm for the samples annealed at 1650°C and 1850°C. For both annealed samples, the absorption coefficient was around 0.1 cm^{-1}, (measured values were 0.114 cm^{-1} for Recipe A, and 0.101 cm^{-1} for Recipe B) which is significantly lower than that of the sample that had not undergone annealing. However, it was not as low as the absorption coefficient of Recipe B which had not undergone any annealing.

It can also be seen that the annealing temperatures gave different absorption coefficients at different wavelengths. Recipe A annealed at 1850°C had a higher absorption coefficient than Recipe A annealed at 1650°C at just below 300 nm, but a lower absorption coefficient at between 500 and 600 nm. This is because different annealing regimes reduce different types of defects that give rise to absorption. Without being bound by theory, it is suggested that Recipe A annealed at 1650°C leads to a significant reduction in the defect responsible for a broad absorption spectral feature which can be described by a λ^{-3} dependence, where λ is the wavelength. Increasing the annealing temperature to 1850°C leads to a reduction in other defects responsible for broad absorption peaks centred at 360 and 520 nm, and a small increase in the peak at 270 nm. The latter spectral feature is due to the presence of the N_s^0 defect, while the other features are tentatively ascribed to vacancy clusters and other defects comprising some or all of nitrogen, lattice vacancies and hydrogen, such as NVH^0, as discussed in J. Phys.: Condens. Matter 25 (2013) 275801.

In order to test the effect of synthesis temperature on absorption coefficient, Recipe C was prepared in the same way as Recipe B, but with a synthesis temperature 60°C lower than that of Recipe B. Figure 6 shows the optical absorption spectra of examples diamonds made using recipes B and C.

It can be seen that the UV-vis optical absorption spectrum of Recipe C is significantly higher than that of Recipe B at wavelengths below around 600 nm. Indeed at 450 nm, the optical absorption of Recipe C is around 0.2 cm^{-1} compared to less than around 0.05 cm^{-1} for Recipe B. Again, this makes the diamond of Recipe B more suitable for use in diamond Raman laser systems operating at 450 nm. However, note that the diamond of Recipe C still has an improved optical absorption at 450 nm compared to the un-annealed diamond made according to Recipe A.

For certain optical applications it is desirable to provide a material which has low optical absorbance and low optical birefringence. Such a material may be engineered by fabricating a single crystal CVD synthetic diamond material which has a low concentration of impurities, which would otherwise increase the optical absorbance of the material, and a low concentration of extended defects which would otherwise introduce anisotropic strain into the diamond lattice structure causing birefringence. Patent literature relevant to such optical grade single crystal CVD synthetic diamond material includes WO2004/046427 and WO2007/066215. Embodiments of WO2004/046427 are described as producing a layer of single crystal CVD diamond having substantially no regions of high birefringence and containing single substitutional nitrogen in a concentration range 3×10^{15} atoms/cm^3 to 5×10^{17} atoms/cm^3 as measured by electron paramagnetic resonance spectroscopy (EPR). Such materials having low and controlled levels of nitrogen and low strain are described as being manufactured using a chemical vapour deposition technique in which low and controlled levels of gas phase nitrogen are introduced into the synthesis atmosphere within a concentration range 300 ppb to 5 ppm.

Diamond synthesized according to Recipe A has been found to have an optical birefringence such that in a sample of the single crystal CVD diamond material having an area of at least 1.3 mm x 1.3 mm, and measured using a pixel size of area in a range 1×1 µm^2 to 20×20 µm^2, a maximum value of $\Delta n_{[average]}$ does not exceed 2×10^{-5}, where $\Delta n_{[average]}$ is an average value of a difference between refractive index for light polarised parallel to slow and fast axes averaged over the sample thickness. Nominally a lower limit for the maximum value of $\Delta n_{[average]}$ may be 1×10^{-7}.

The optical birefringence is measured along the direction of pump or Stokes beam propagation, as this is most relevant to the single crystal CVD diamond when used in a diamond Raman laser system. This may be perpendicular to the growth direction of the single crystal CVD diamond material as dislocations tend to propagate through the material in the growth direction, and will represent the direction having the highest birefringence of the sample.

Figure 7 shows birefringence measured for a CVD single crystal diamond made according to Recipe B. Figure 7a shows the birefringence measured in a direction parallel to the growth direction, and has a Δn_{max} of 1.7×10^{-4}. Figure 7b shows the birefringence measured in a direction perpendicular to the growth direction, and has a $\Delta n_{max} = 1.58 \times 10^{-6}$. The sample size in each case was approximately 2 x 2 x 2 mm.

While this invention has been particularly shown and described with reference to embodiments, it will be understood by those skilled in the art that various changes in form and detail may be made without departing from the scope of the invention as defined by the appended claims.

CLAIMS

1. A diamond Raman laser system, the system comprising:

a laser for providing laser light having a wavelength less than 750 nm, the laser comprising at least one pump laser and further comprising a Raman oscillator, the at least one pump laser and the Raman oscillator being configured to provide an n-order Raman oscillation, where n is an integer;

wherein the Raman oscillator comprises single crystal diamond, the single crystal diamond having an optical absorption coefficient measured by optical spectroscopy at 450 nm of less than 0.5 $cm^{-1.}$

2. The diamond Raman laser system according to claim 1, wherein the single crystal diamond has an average optical birefringence, measured at 20°C along the direction of pump or Stokes beam propagation, such that the birefringence over at least 80% of the cross-sectional area does not exceed 2 x 10^{-5}.

3. The diamond Raman laser system according to claim 1 or claim 2, wherein the single crystal diamond has an optical absorption measured by optical spectroscopy at 450 nm selected from any of less than 0.3 cm^{-1}, less than 0.2 cm^{-1} and less than 0.1 cm^{-1}.

4. The diamond Raman laser system according to any one of claims 1 to 3, wherein the single crystal diamond comprises a single substitutional nitrogen, N_s^0, concentration as measured by electron paramagnetic resonance, EPR, selected from any of less than 100 ppb, and less than 50 ppb.

5. The diamond Raman laser system according to claim 4, wherein the single crystal diamond comprises a single substitutional nitrogen, N_s^0, concentration as measured by electron paramagnetic resonance, EPR, selected from any of greater than 5 ppm and greater than 10 ppb.

6. The diamond Raman laser system according to any one of claims 1 to 5, wherein the diamond Raman laser system has an operating power selected from any of at least 200 W, at least 500 W, at least 1000 W, and at least 1500 W.

7. The diamond Raman laser system according to any one of claims 1 to 6, wherein the diamond Raman laser system has a beam parameter product selected from any of less than

60 mm·mrad, less than 40 mm·mrad, less than 20 mm·mrad, less than 10 mm·mrad, and less than 5 mm·mrad.

8. The diamond Raman laser system according to any one of claims 1 to 7, wherein the laser has a Stokes wavelength in a range selected from any of 240 to 700 nm, 300 to 600 nm and 400 to 500 nm.

9. The diamond Raman laser system according to any one of claims 1 to 8, wherein the pump laser comprises at least one laser diode.

10. The diamond Raman laser system according to any one of claims 1 to 8, wherein the pump laser comprises a plurality of laser diodes.

11. The diamond Raman laser system according to claim 10, wherein the plurality of laser diodes are coupled together by optical fibre.

12. The diamond Raman laser system according to any one of claims 1 to 11, wherein the single crystal diamond is selected from any one of chemical vapour deposition, CVD, diamond, high pressure high temperature, HPHT, diamond, and natural diamond.

13. The diamond Raman laser system according to any one of claims 1 to 12, wherein the single crystal diamond has an anti-reflective surface coating.

14. The diamond Raman laser system according to any one of claims 1 to 13, wherein the single crystal diamond has been annealed at a temperature of at least 1400°C to reduce the absorption coefficient.

15. The diamond Raman laser system according to any one of claims 1 to 14, further comprising a heat sink in thermal contact with the single crystal diamond.

16. The diamond Raman laser system according to any one of claims 1 to 15, wherein the single crystal diamond forms a first layer in a composite single crystal diamond, the composite single crystal diamond further comprising a second layer of single crystal diamond, the second layer having a higher single substitutional nitrogen concentration than the first layer.

17. The diamond Raman laser system according to claim 16 where dependent on claim 15, wherein the composite single crystal diamond comprises a third layer of single crystal diamond embedded in the heat sink.

18. The diamond Raman laser system according to any one of claims 1 to 17, wherein the diamond has a linear dimension in the path of the laser of at least 2 mm.

19. Use of a diamond Raman laser system according to any one of claims 1 to 18.

20. Use of a diamond Raman laser system according to claim 19, wherein the diamond Raman laser system is used for processing materials having a low infra-red absorption.

21. Use of a diamond Raman laser system according to claim 20, wherein the diamond Raman laser system is used for processing any of copper and platinum.

22. Use of a diamond Raman laser system according to claim 20 or 21, wherein the use comprises any of machining and welding.

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Claims searched:	all	**Date of search:**	13 January 2022

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
Y	1 -22	WO 2005/057740 A2 (SPECTRA SYSTEMS CORP) see Figure 1 and Table 2 and para. 0019
Y	1 -22	US 2020/0180080 A1 (ZEDIKER) see Figures 13A and B and Table III and para 0098
Y	1 -22	WO 2020/107030 A1 (NUBURU INC) see Figure 3 and para 0048
Y	1-22	WO 2013/067599 A2 (UNIV MACQUARIE) see Figures 8A and B and paras.
Y	1 -22	WO 2016/033343 A1 (NUBURU INC) see Figure 17 and Table III and para 0096
Y	1 -22	GB 2476478 A (ELEMENT SIX LTD) see Figures 2-5 see whole document
Y	1 at least	GB 2477188 A (ELEMENT SIX LTD) see Figures 1-3 see whole document
Y	Y 1-22	https://en.wikipedia.org/wiki/Raman_Laser see Section on "Specific Properties of Lasers"

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The following online and other databases have been used in the preparation of this search report

WPI, EPODOC, Patent Fulltext

International Classification:

Subclass	Subgroup	Valid From
H01S	0003/30	01/01/2006
C01B	0032/26	01/01/2017
C23C	0016/27	01/01/2006
C30B	0029/04	01/01/2006
H01S	0003/06	01/01/2006
H01S	0003/0941	01/01/2006
H01S	0003/16	01/01/2006
H01S	0005/30	01/01/2006