Multiplex coherent anti-stokes Raman spectroscopy on a CMOS compatible platform

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Coherent anti-stokes Raman spectroscopy (CARS) is a nonlinear enhanced Raman technique in which the Raman signal is driven by the beating of pump and probe beams. It has a much higher sensitivity compared with traditional Raman technique and it is widely used for bio-sensing. However current CARS based on confocal microscopy involves bulky and complex instrumentations. To facilitate the miniaturization and improve the sensitivity, multiplex CARS (M-CARS) on chip is proposed in this article. The scheme of M-CARS is clarified and possible challenges are discussed.

Introduction

Coherent anti-Stokes Raman scattering (CARS) is a nonlinear coherent variation of Raman spectroscopy where two beams of frequency ω_p (pump) and ω_s (Stokes) are injected into a Raman active material to generate a new beam at $\omega_a = 2\omega_p - \omega_s$ (anti-Stokes). CARS provides orders of magnitude enhancement over spontaneous Raman spectroscopy and it is free from fluorescence. CARS microscopy has now been widely used for molecule identification[1], macromolecular structure determination[1] and combustion analysis[2]. However most CARS systems relies on the tight focusing condition provided by confocal microscopy system with high numerical aperture objectives. Dictated by its size and complexity, cofocal CARS setup is less suitable for complex environment and in-situ detection. We believe lab-on-a-chip sensing based on integrated photonics platform could facilitate exploring the full potential of CARS. CARS-on-chip could be advantageous over microscope in (1) enhanced detected signal by long interaction length [3], (2) in-situ operation and real-time monitoring, (3) guided and safe laser power deliver.

We here propose a multiplex CARS device based on silicon nitride chip. The device is capable of generating the broadband stokes wave on chip and even the source and spectral detection could in principle also be integrated on the same chip.

Multiplex Coherent anti-Stokes Raman spectroscopy

In four-wave mixing processes, two beams, pump and signal, are injected into the nonlinear material to generate an idler beam. The process is usually mediated by the anharmonicity of bound electron coined as Kerr nonlinearity $\chi^{(3)}_{kerr}$. It is worth mentioning the Kerr response is spectrally flat over the spectral region we are concerned.

In Raman active material the nonlinear response of vibration bond $\chi^{(3)}_R$ could also mediate the four-wave mixing process and it constitutes CARS. Unlike Kerr effect, CARS is strong only when the frequency difference between a pump and probe corresponds to

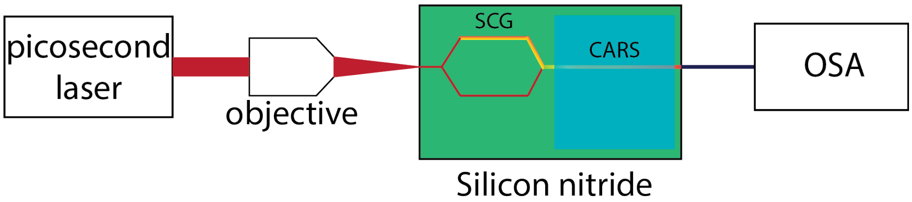

Figure 1: Proposed schematic setup for on-chip MCARS. The green box indicates the silicon nitride chip and the blue box inside is the waveguide that exposed to analytes.

the intrinsic frequency of molecular vibration modes. Thus by fixing the pump frequency and sweeping the Stokes wave we can record an idler spectra with features corresponding to vibration frequencies. As these features vary from bonds to bonds, they constitute the fingerprints of molecules and are widely adopted for molecule classification and identification. It is worth noticing CARS is always accompanied by Kerr effect, which creates the so-called non-resonant background and should be removed afterwards.

As the vibration modes of a molecule spans over 1000 cm^{-1} from the pump, the probe should be either tunable over large spectral range or ultra-broadband to cover the range. Broadband stokes enabling multi-element acquisition in a single pulse is referred to as multiple-CARS (MCARS)[4]. As the broadband source can be generated via nonlinear broadening with high brightness and tailorable spectral coverage, MCARS is more suitable for integrate photonics platform.

Our proposed MCARS setup is plotted in Fig. 1. A picosecond pulsed laser is injected into silicon nitride chips through an objective. Part of the input is tapped for supercontinuum generation and later combined with the rest. The combined wave are then injected to waveguides exposed to analytes for anti-Stokes wave generation. The generated spectra is then analyzed in an optical spectrum analyzer.

As MCARS is a phase-sensitive nonlinear process, it requires phase-matching condition to be efficient. In addition, the tailoring of nonlinear spectral broadening also requires specific phase matching condition. These two requirements direct us first into the dispersion engineering of the waveguide.

Dispersion engineering and Supercontinuum Generation

Phase matching condition can be viewed as momentum conservation $2k_p = k_s + k_a$ in nonlinear processes. It is usually interpreted in terms of group velocity dispersion (GVD) $D = {}^{-2\pi c}/_{\lambda} \cdot {}^{\partial^2 k}/_{\partial\omega^2}$. GVD for our silicon nitride waveguide is composed of two contributions, the intrinsic material dispersion D_M and the geometrical dispersion D_W influenced by waveguide structure. As the material dispersion is determined in deposition, the general target of dispersion engineering is tuning the waveguide geometry to tailor the total GVD.

For an efficient MCARS process within a waveguide of 1 cm-long, if we would like to observe Raman vibration up to 2000 cm^{-1}, it is preferable to have $|D| < 100$ ps/nm/km. However for the wavelength range interested as pump (~ 785 nm) the material dispersion possesses strong normal dispersion ($D \approx -630$ ps/nm/km) so it requires strong waveguide dispersion with opposite sign for MCARS. The requirement of strong waveguide dispersion asks for innovative design of waveguide geometry. Inspired by [5, 6] we de-

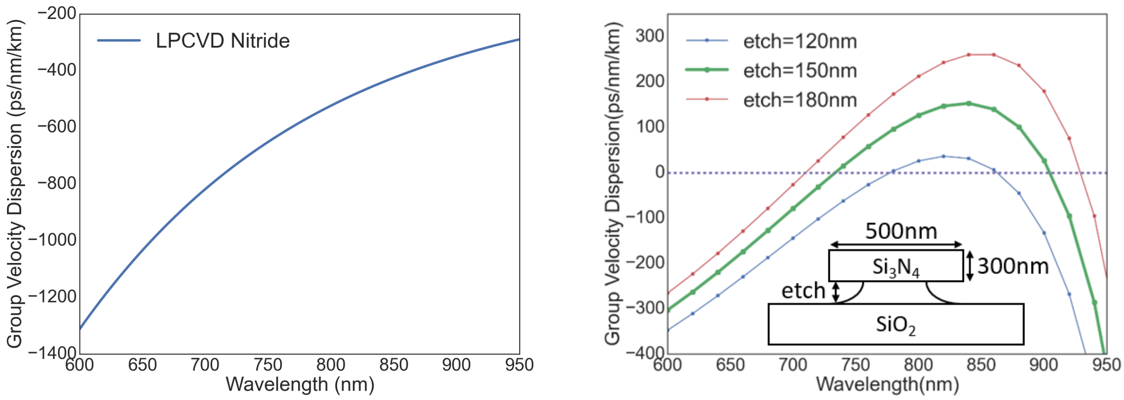

Figure 2: (Left) Dispersion of LPCVD silicon nitride material. (Right) Dispersion of engineered waveguide

vice a waveguide with underetched silicon dioxide undercladding. The dispersion of the underetched waveguide is shown in the right panel of Fig.2.
With the underetched waveguide we proceed immediately to the nonlinear spectral broadening part of MCARS. The drastic spectral broadening is also called supercontinuum generation (SCG) and it is useful not only in MCARS but also in frequency metrology [7] and optical coherence tomography (OCT) [8]. With the underetched waveguide, we have successfully demonstrated [9] an supercontinuum ranging from 488 nm to 978 nm pumped at 795 nm with 874 W coupled peak pump power as shown in Fig.3. To the best of our knowledge, this is the first demonstration of an octave spanning supercontinuum extending in the sub-500 nm wavelength range on an integrated platform, forming a solid first step on on-chip MCARS. With the success of SCG, the CARS is now under investigation and we expect to have the preliminary result soon.
The current dispersion engineering technique has however a restriction on the scope of application of MCARS. The Raman active material needs to be a thin layer ($<$ 30 nm) functionalized on the waveguide surface to maintain proper dispersion. Although a wide range of analyst could be detected in this way, we would still like to retain the full capacity of MCARS on aqueous environment. To fully explore the capacity of MCARS, we are also actively developing waveguide for quasi-phase matching technique, including width modulation and subwavelength grating waveguide.

Conclusion

We have proposed a novel scheme for multiplex coherent anti-Stokes Raman spectrscopy, which could potentially enhance the sensitivity over microscope-based system for orders of magnitude. The critical step of dispersion engineering has been done and the procedure of CARS experiment has been clarified. With the dispersion engineered waveguide we have also successfully demonstrated a first visible octave spanning SC on silicon nitride platform.

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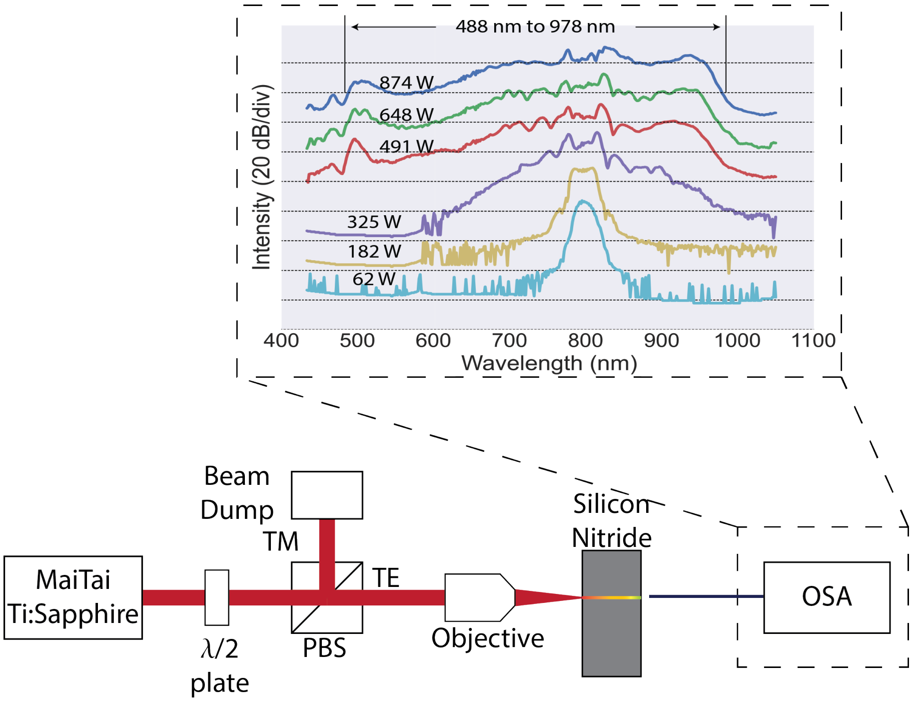

Figure 3: SCG based on underetched waveguide. Light is coupled in through a microscope objective and coupled out through a lensed fiber. The peak power of pump coupled into the waveguide is also specified in the figure.

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