Spontaneous Raman Emission and Tunable Stokes Shift in Porous Silicon

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Abstract- In this paper, in order to generate radiation at 1.54 micron, an approach based on Raman scattering in porous silicon is presented. Experimental results, proving spontaneous Raman emission at 1.5 micron and tuning of the Stokes shift, are reported.

I. INTRODUCTION

The Raman effect in silicon is more than 10,000 times stronger than in glass fiber, making silicon an advantageous material. Instead of kilometres of fiber, only centimetres of silicon are required. However, 'Raman amplification' is a small effect, and to build a laser with it you need a very high power intensity and very low absorption losses [1]. Such conditions have already been achieved in optical devices made in silica (SiO\textsubscript{2}), whereas, in silicon on insulator structure, Raman amplification was limited to very short pulses of a few nanoseconds at most [2,3,4]. The problem is that an unwanted nonlinear side effect - two photon absorption- creates pairs of electrons and holes that remain for a long time in the sample and absorb both the pump and light and signal light, and so quickly turn off the Raman amplification. Rong et al [5] solve this problem by embedding the silicon waveguide within a reverse-biased p-i-n junction diode, designed to extract electrons and holes away from the waveguide. With this design, they demonstrate a silicon laser with continuous operation.

However spectral limitation of the Raman effect in silicon are unavoidable in the SOI platform. In the case of Raman amplification, the limited bandwidth of the spontaneous Raman signal from silicon (105 GHz) makes it unsuitable for its use in broad band WDM applications, unless the multi-pump schemes are implemented.

In this paper, an approach based on Raman scattering in porous silicon is discussed. This approach present some advantages:
- spectral broadening of spontaneous Raman scattering with respect to silicon is achieved.
- infiltrating liquids in porous silicon a tuning of the Stokes shift is achieved.

II. SPONTANEOUS RAMAN EMISSION

In Raman scattering both energy and momentum are conserved. Ideal crystal translation symmetry leads to plane wave phonon eigenstates. Due to the small wavevector of the optical photons, the phonons in the Raman scattering of crystals have very small momentum compared with the Brillouin zone. So, the phonons involved in first-order Raman scattering have q=O and they are at the center of the Brillouin zone (Γ point).

The Raman effect in silicon is due to the scattering of the light by the optical phonons of the crystals. The strongest Stokes peak (first order) is due to the scattering from the threefold degenerate optical modes at the center of the Brillouin zone. It lies at 15.6 THz with a FWHM of 105 GHz at room temperature.

In presence of disorder finite size effects or when the crystalline size becomes very small, quantum confinement relaxes the q=O rule and phonons at q\neq0 become Raman active leading to a downshift and broadening of the Raman peak. The phonon peak broadens towards lower energy and shifts slightly. The line-shape asymmetry increases as the incident photon energy is increased [6-16].
Figure 2. Comparison of Raman Spectra measured in silicon and porous silicon sample.

while porous silicon sample is obtained by an electrochemical etching starting from p+ silicon wafer. The monolayer realised has a porosity p=70% and a thickness d=3 micron. The measures are carried out at room temperature.

Being the characteristic of Raman scattering in silicon sample well known, in order to test our experimental set up, we carried out some preliminary measures on silicon. Fig. 2 shown the Raman spectra measured in silicon sample. It is symmetric and is in excellent agreement with the value of the optical phonon frequency in silicon. In fact it has a peak at 1542 nm, corresponding at 15.7 THz red-shifted from the pump wavelength.

In order to point out the principal difference with respect to silicon sample, in Fig. 2 is also shown the Raman spectra measured in porous silicon sample. We note that also in the case of porous silicon the observations are in excellent agreement with the behaviour described by the theory. Due to the small crystalline size, quantum confinement relaxes the q=0 rule and phonons at q≠0 become Raman active as a consequence the phonon peak broadens towards lower energy and shifts slightly. We note that a significant spectral broadening is obtained due to the nanostructure of porous silicon.

In Fig. 3, the measured spontaneous Raman back scattering from porous silicon sample at increased incident power are reported. The incident powers onto the sample are 0.5 W and 1W respectively. It is important to point out that as expected from theory the spontaneous Raman is a linear effect.

III. TUNABILITY OF SPECTRA

Adsorption and wetting phenomena are due to the action of molecular interactions between a fluid and the adsorbent, which is usually considered to be rigid. In the adsorption phenomena the adsorbent also experiences the action of the molecular forces, and some substrate deformation must exist, as indeed revealed by numerous observation of adsorption strains. Measurements of adsorption strains in porous silicon are actually of great interest, however in our case they are useful in order to prove the possibility to tune the Stokes shift [17]. In fact, Raman scattering can be used to measure strain induced in substrate. Compressive stress will result in an increase of the Raman frequency shift, while tensile stress results in a decrease.

When PS is exposed to vapour, capillary condensation in the silicon pores have been observed [18]. When the vapour is stable in a large volume, the liquid phase can condense in a confined volume, and is then separated from the vapour phase by a concave spherical meniscus [17]. The maximum capillary stress ΔP occurs when the meniscus enter the pores and it is given in first approximation by the Laplace equation

$$\Delta P = 2\gamma_s/\rho$$

where γs is surface tension of the liquid and ρ is the pore radius. In this situation, inside the pore, there is a negative pressure in the liquid leading to a contraction of the adsorbent. The isotropic strain ε is given by

$$\epsilon = -\Delta P / 3K = -2\gamma_s / 3Kr$$

where K is the bulk modulus of a macroscopic sample.

In this experiment we use a porous silicon microcavity (PSM) obtained by electro-chemical etching on p+ type (ρ=8-12mΩ cm) standard silicon wafer. In order to realise a cavity a λ/2-thick defect has to be placed in between two distributed Bragg reflectors (DBRs). The DBR structures are made alternating high and low porosities layers with 57 and 79% porosity, respectively. The total PSM thickness is 5 micron. In p+ type silicon wafer, the pores have an anisotropic cylindrical structure of about 10 nm diameter, with axis parallel to the (001) direction.

Raman spectra are measured in backscattering configuration using a diode laser at 404 nm. The experiment has been carried out in an “out-of- resonance configuration”, both for excitation and Raman radiations, and using a low power laser radiation (about 10mW). Moreover, we note that all spectra are obtained by normalization of the measured reflected signals with respect to the laser signal. Finally, the location of the Raman peaks are obtained fitting the experimental results
by a Lorentzian curve.

The first step was the measure of the normalised Raman spectra in unperturbed porous silicon microcavity. Fig. 4 shows the results. The measured peak is at about 413.6 nm, this result is in agreement with the shift, with respect to the pump wavelength, due to the optical phonon frequency in porous silicon (corresponding at 15.7 THz red-shifted).

Afterwards, with the aim of study the influence of the chemical species infiltration in PS, a small amount of volatile liquids were added to the vial containing the PSM. The vapors saturated rapidly the vial atmosphere, after that the acquisition of spectra were carried out. In Fig. 5 is shown the experimental Raman spectra for pentane. Fitting the experimental results with a Lorentzian profile, the Raman peak is obtained at about 409.1 nm. So, we measure a shift of Raman spectra with respect to the unperturbed case of about 4 nm for pentane. We note that the Raman shift is reversible.

Of course, choosing a liquid with a different surface tension ($\gamma_S$), a different shift could be achieved (see Eq. (2)), therefore the Raman spectra could be tunable.

V. CONCLUSIONS

In this paper we report experimental results proving spontaneous Raman emission and tuning of the Stokes shift in porous silicon. We measure a significant spectral broadening of spontaneous Raman scattering with respect to silicon and a shift of the Stokes scattering of about 4 nm infiltrating pentane in porous silicon. Future investigations concerns the study on nonlinear phenomena in order to exploit the possibility to realise an amplifier in porous silicon based on Raman scattering.

REFERENCES

[1] J. Faist, Nature, vol. 433, 2005, pp.691-692
[2] S. M. Spillane, T. J. Kippenberg K. J. Vahala, Nature, 415, 2002, pp.621-626
[3] O. Boyraz, B. Jalali, Optics Express, 12, 2004, 5269-5273
[4] H. Rong et al., Nature, 433, 292-294 (2005)
[5] H. Rong et al., Nature, 433, 292-294 (2005)
[6] T. Canham. “Nanostructured silicon as an active optoelectronic material. In Frontier of Nano-Optoelectronic Systems”, Edited by L. Pavesi and E. Buzaneva. Kluwer Academic Publishers (2000), 85-98.
[7] R. Tsu, H. shen and M. Dutta. “Correlation of Raman and photoluminescence spectra of porous silicon.” Appl. Physics lett. 60 (1), 1992, pp.112-114.
[8] R. Tsu, H. shen and M. Dutta. Appl. Physics lett. 60 (1), 1992 pp. 112-114.
[9] J. M. Perez., J. Villalobos,P. McNeill, J. Prasad, R. Cheek and J. Kelber, J. P. E. P. D. stevens and R. Glosser. Appl. Physics lett. 61 (5) 1992, 563-565.
[10] G. Mariotto, F. Ziglio, F. L. Freie Jr. Journal of non crystalline solids 192 & 193 (1995) 253-257.
[11] Z. Sui., P. P. Leong, and I. P. Herman. Appl. Physics Lett. 60 (17), 1992, pp. 2086-2088.
[12] S. L. Zhang, Y. Hou and K. S. Ho, B. Qian and S. Cail. J. Appl. Phys. 72 (9), 1992, pp.4469-4471.
[13] J. D. Moreno, F. Aguillo-Rueda, E. Montoya, M. L. Marcos and J. Gonzales-Velasco, R. Guerrero-Lemus and J. Martinez-Duart. Appl. Physi. Lett, 71, 13 1997, pp.2166 2168.
[14] F. Kozlowski, W. Lang. Appl. Physic. Lett, 1992pp.5401-5408.
[15] H. Ritcher, Z. P. Wang and L. Ley. The one phonon Raman spectrum in microcrystalline silicon. Solid State Communications. 39, (1981), 625-629
[16] H. Campbell and P. M. Fauchet. The effects of microcrystal size and shape on the phonon Raman spectra of crystalline semiconductors. Solid State Communications. 58, (1986), 739-741.
[17] G. Dolino, D. Bellet, and C. Faivre, “Adorption strains in porous silicon”, Physical Review B, vol. 54, No. 24, 1996.
[18] A.V. Neimark, P.I. Ravikovitch, Micro. Meso. Mat. 44-45 (2001) 697-707