Coherent Backscattering of Raman Light

Barbara Fazio [1‡], Alessia Irrera [1‡], Stefano Pirotta [2‡], Cristiano D'Andrea [3,4§], Salvatore Del Sorbo [2], Maria Josè Lo Faro [1,3,5], Pietro Giuseppe Gucciardi [1], Maria Antonia Iatì [1], Rosalba Saija[6], Maddalena Patrini [2], Paolo Musumeci [3,5], Cirino Salvatore Vasi [1], Diederik S. Wiersma[7,8,9], Matteo Galli [2*] and Francesco Priolo [3,4,5,10*]*

[1] CNR-IPCF, viale F. Stagno d'Alcontres 37, Faro Superiore, 98158 Messina, Italy.

[2] Dipartimento di Fisica, Università degli Studi di Pavia, via Bassi 6, 27100 Pavia, Italy.

[3] MATIS IMM-CNR, via S. Sofia, 64, 95123 Catania, Italy.

[4]CSFNSM, Viale A. Doria, 6, 95125 Catania. Italy

[5] Dipartimento di Fisica e Astronomia, Università di Catania, via S. Sofia, 64, 95123 Catania, Italy.

[6] Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra, Università di Messina, I-98166 Messina, Italy

[7] LENS, Università di Firenze, via Nello Carrara, 1, 50019 Sesto Fiorentino (Firenze), Italy.

[8] Dipartimento di Fisica e Astronomia, Largo Enrico Fermi, 2 , 50125 Firenze, Italy.

[9] INRIM - Istituto Nazionale di Ricerca Metrologica, Strada delle Cacce, 91, 10135 Torino, Italy

[10] Scuola Superiore di Catania,Università di Catania, via Valdisavoia, 9, 95123 Catania, Italy.

*** Corresponding authors:** e-mail address: fazio@ipcf.cnr.it, Tel.: +39 090 39762246; fax: +39 090 3974130; e-mail address: matteo.galli@unipv.it , Tel. +39 0382 987686, fax: +39 0382 987563, e-mail address: francesco.priolo@ct.infn.it , Tel.: +39 095 3785401; fax: +39 095 3785243;

‡ These authors contributed equally

§ Now at CNR-IFAC, via Madonna del Piano 10, I-50019 Sesto Fiorentino (Firenze), Italy.

Coherent backscattering of light (CBS) is observed when electromagnetic waves undergo multiple scattering within a disordered optical medium. So far, CBS has been studied extensively for elastic (or Rayleigh) light scattering. The occurrence of inelastic scattering affects the visibility of the backscattering effect by reducing the degree of optical coherence in the diffusion process. Here we discuss the first experimental observation of a constructive interference effect in the inelastically backscattered Raman radiation from strongly diffusing silicon nanowire random media. The observed phenomenon originates from the coherent nature of the Raman scattering process, which typically occurs on a scale given by the phonon coherence length. We interpret our results in the context of a theoretical model of mixed Rayleigh-Raman random walks to shed light on the role of phase coherence in multiple scattering phenomena.

The transport of light in disordered materials drives several exciting fundamental effects that originate from multiple scattering and wave interference, such as Anderson localization and random lasing[1-7]. One of the most striking phenomena related to the diffusion of electromagnetic waves in random optical media is the coherent backscattering of light, a robust interference effect that is due to the coherent superposition of counter-propagating multiply scattered waves[8-10]. It manifests macroscopically through the observation of an enhanced light intensity at small angles around the backscattering direction, known as the backscattering cone, and can be considered the optical equivalent of weak localization observed in disordered electronic systems[11]. Coherent backscattering (CBS) has been studied for light waves in a number of physical systems, ranging from high refractive index powders[12] to cold atom gases[13,14], liquid crystals[15], human bones[16], biological tissues[17] and many other randomly textured materials.

Recently, CBS was proposed as a useful tool to probe the scattering properties at a depth inside materials, as such properties are closely related to the structural heterogeneities of the considered medium[16,17].

The robustness of the CBS effect against disorder is based on the phase coherence between the incoming and the outgoing waves in a scattering process, which for *elastic* light scattering such as Rayleigh scattering can be preserved even after a very large number of scattering events. Conversely, *inelastic* scattering processes for which energy and phase are not conserved causes a reciprocity symmetry breaking; inelastic processes are known to strongly affect the CBS intensity by inducing its incoherent reduction, as extensively studied for the case of both classical[18,19] and quantum waves[20-22]. Spontaneous Raman scattering in condensed matter, where an optical pump wave is inelastically scattered within a material by creation or annihilation of quanta of vibrations (phonons), is usually considered one of such incoherent processes. Nevertheless Raman scattering is fundamentally coherent in origin, indeed in the scattering process the pump wave, the Stokes/anti-Stokes wave and the lattice vibration are phase locked meaning that the frequency and phase of the phonons populating the vibration mode must be equal to the beating frequency and phase of the overlapping laser and Raman local fields[23]. However, coherence is quickly lost after short times of few picoseconds and over short distances of tens of nanometres, which are typical values for the phonon coherence time and length in solid-state materials. The loss of coherence results in a macroscopically incoherent behaviour of the Raman scattered light, as it is usually measured in experiments. The spatial coherence of spontaneous Raman scattering was recently observed in the near-field regime, probing the Raman signal with sharp tips on a length scale much smaller than λ and comparable to the phonon coherence length[24]. On the other hand, the temporal coherence of spontaneous Raman

scattering was investigated through Transient Coherent Ultrafast Phonon Spectroscopy (TCUPS), which employs ultrafast laser pulses on the order of 10 fs (thus much shorter than the phonon coherence time[25]). We also note that quantum interference effects between Raman transitions in atomic systems that result in an anti-enhancement of CBS, which can be seen as the optical analogue of weak anti-localization in electron transport, have been theoretically predicted[26,27], suggesting that the CBS phenomenon can show a more complex behaviour than that associated with an enhanced cone of backscattered intensity. In this article, we show – for the first time to our knowledge – that the coherent nature of spontaneous Raman scattering in condensed matter can be studied at a macroscopic scale through the observation of an enhanced backscattering cone in a simple backscattering experiment, that is, without recurring to ultrafast techniques. The experimental evidence reported in this work is theoretically explained in terms of a mechanism involving reciprocal 'hybrid' Rayleigh-Raman paths inside a strongly scattering medium, where optical coherence is ensured by the symmetry of the Raman tensor and by the short dwell time of light inside the material.

Coherent backscattering from dense nanowire arrays

We consider vertically aligned silicon nanowires (Si NWs) randomly organized in two dimensions as a scattering material exhibiting enhanced spontaneous Raman signal. Specifically, we investigated two Si NW samples: sample 1 (Fig.1a,1b) displays a dense distribution of thin vertically aligned NWs (with a diameter of few nanometres)[28-30], whereas sample 2 (Fig.1c,1d) is characterised by a less dense distribution of NWs with a larger average diameter (tens of nanometres)[31,32] (see Methods for further fabrication details).

To assess the scattering strength of the Si NW samples quantitatively, we measure the Elastic (i.e. Rayleigh) Coherent Backscattering (hereafter ECBS) intensity[33-35]. The accurate determination of the specific angular shape of the ECBS profile provides information not only on the scattering strength of the medium, but also on the path length distribution of light inside the sample. The contribution at the cusp of the ECBS cone is mainly due to long scattering paths involving a large number of scattering events, while its angular width may be expressed as $W \approx 1/k\ell_t$, where k is the light wavevector and ℓ_t is the transport mean free path of light in the medium. The ECBS cones measured at an excitation wavelength λ_{exc}=532 nm for sample 1 and sample 2 are shown in Fig. 1e and Fig. 1f, respectively (the detailed measurement procedure is given in the Methods). The ECBS cones of both samples are characterised by a pronounced rounding of the tip due to the combined effect of light absorption and finite thickness of the Si NW layer, which strongly suppress the contribution of very long paths to the backscattering intensity. Model fits to the data are given by the red lines in Fig. 1e and Fig. 1f, and yield very small values for the transport mean free path: ℓ_t = 0.169 μm and ℓ_t = 0.483 μm for sample 1 and sample 2, respectively (see Table 1 and Supplementary Information Section S1 for details on fit procedures and parameters).

Raman Coherent Backscattering

We then explore the angular dependence of Raman-shifted light from the Si NWs in both samples. We optically pump sample 1 at three laser wavelengths (488 nm, 532 nm and 785 nm), covering the range for which the Si NW medium is characterised by inelastic (absorption) mean free paths spanning lengths between few microns and few tens of microns. Furthermore, we investigate the response (at λ_{exc}=532 nm) of sample 1 after the introduction of silicone oil (with

refractive index 1.46) in the interstices between individual Si NWs: the addition of silicone oil lowers the refractive index mismatch at the Si NWs/air interfaces, leading to a substantial reduction of the scattering strength. The experimental data are shown in Fig. 2, where the Raman backscattering signals (dark yellow dots) are compared to the corresponding ECBS cones (blue dots). We see that the Raman cones display a more rounded tip and a lower enhancement factor with respect to the ECBS ones, although the shapes of the two curves are more similar at large scattering angles. Moreover, for increasing excitation wavelengths we observe a clear reduction of the Raman backscattering signal as compared to the corresponding ECBS signal (Fig. 2a,b,c). In Fig. 2d ECBS and Raman cones excited at 532 nm after the introduction of silicone oil are shown. The data related to sample 2 at λ_{exc}=532 nm are shown in Fig. S2.1 of Supplementary Information Section S2.

The behaviour of the Raman backscattered intensity indicates that a subtle multiple scattering phenomenon must be taking place for Raman light diffusing within the dense Si NW samples. To further support this observation, and to rule out any possible spurious effect due to the anisotropy of the NWs layer (such as shadowing effects), we measure the angle-dependent photoluminescence (PL) emission from the Si NWs. Indeed, the bright PL emission, peaked at λ_{PL} = 690 nm, is readily observed from our Si NW sample 1 due to the quantum confinement effect[29]. As the broad PL emission extends well below the Raman Stokes wavelength, which is visible in the measured Raman spectra as a smooth decaying background (as shown in Fig 3a), we perform a simultaneous measurement of Raman and PL emission . This ensures that both datasets are acquired under the same experimental conditions. The backscattered intensities of the Raman and PL signals can then be compared by integrating the spectra over a narrow wavelength range (around the Raman peak), indicated in Fig. 3a as the blue and pink areas

138 respectively. The outcome of the integration is shown in Fig. 3b, and it confirms the presence of
139 a Raman-enhanced backscattering cone against a simple diffusing (Lambertian) PL emission –
140 the latter being an incoherent process in its spontaneous form.
141 The observed behaviour for the Raman backscattered light in Si NW media strongly suggests the
142 occurrence of a *coherent* effect where the Raman Stokes waves interfere constructively in the
143 backscattering direction, in analogy to the well-established ECBS effect for Rayleigh scattered
144 light. Raman waves are generated inside the material within a random walk of the pump beam
145 that is typically few microns long, as deduced from the ECBS results on the investigated
146 samples. However, how is coherence with the pump beam preserved given the extremely short
147 coherence length of the lattice vibrations, which is much shorter than a typical random walk?
148 How does reciprocity of optical paths hold for Raman scattered light? To answer these questions
149 we consider the situation schematically represented in Fig. 4a. Here, a pump beam I enters the
150 sample as a Rayleigh wave and after being elastically scattered several times gives rise to a
151 Raman scattered wave at an arbitrary point ***R***. The generated Stokes-shifted wave is then
152 multiply scattered within the sample and exits as a Raman beam S (solid blue-red line in figure).
153 We are then left with a hybrid Rayleigh-Raman scattering path, which may be thought of as the
154 actual random walk for Raman scattered light. Now, for any of such *direct* hybrid path it exists a
155 *reverse* hybrid path (dashed blue-red lines, corresponding to the pump I' and the Raman S'
156 beams, respectively), as obtained by reversing the propagation direction and also by exchanging
157 the Rayleigh-Raman random walks. In general, these two hybrid paths accumulate a random
158 phase difference within their random walks, which in turn makes the outgoing Raman beams S
159 and S' mutually incoherent. Moreover, polarization of these two hybrid paths may also not be
160 conserved due to the presence of an inelastic scattering event at ***R***. We show, however, that if the

Stokes shift introduced by Raman scattering is small compared to the Rayleigh wavelength then both polarization and phase coherence between the hybrid paths is preserved, restoring reciprocity and enabling the coherent superposition of the outgoing backscattered Raman fields. A detailed representation of the Raman scattering event occurring at $\boldsymbol{R}$ is given in Fig. 4b,c for the direct (left) and reverse (right) hybrid paths. The corresponding scattering cross-sections for the two processes are also shown, where $R(\omega_i, \omega_s)$ denotes the second-rank Raman tensor. If we now consider $\omega_i \approx \omega_s$, as is usually done in Raman theory, the Raman tensor $R(\omega_i, \omega_s)$ becomes *symmetric* with respect to the exchange of the polarization versors $\boldsymbol{e}_i$ and $\boldsymbol{e}_s$[36-39]. The assumption $\omega_i \approx \omega_s$ implies that $\boldsymbol{k}_i \approx \boldsymbol{k}_s$ (and $\boldsymbol{k}'_i \approx \boldsymbol{k}'_s$), thus making the *same* phonon mode (ω_q, $\boldsymbol{q}$) equally available for both scattering paths (Fig. 4d). This has the additional important consequence that the random phase jump introduced by the creation/annihilation of a phonon is exactly cancelled out when considering the phase difference between reciprocal paths. We point out that this last statement is strictly true provided that the dwell time for the two reciprocal paths is much shorter than the phonon coherence time. In our case, due to the very short transport mean free path (deduced by the ECBS cones) and to the strong material absorption, we estimate an average dwell time of the order of few femtoseconds (corresponding to an average total scattering path of few microns), which is far below the 1 picosecond phonon coherence time in crystalline silicon[40,41].

In the light of these considerations, we are entitled to assert that multiple Raman scattering within our Si NWs may be described by hybrid Rayleigh-Raman scattering paths for which: i) reciprocity holds true, ii) coherence with the pump beam is preserved and iii) the observed Raman-enhanced cone is indeed due to the constructive interference in the backscattering direction of Raman-shifted waves that are *coherently* generated in a multiple

scattering process. We shall refer to the observed phenomenon as Raman Coherent Backscattering (hereafter RCBS), in analogy with the ECBS effect for Rayleigh scattered light.

Dephasing mechanism and enhancement factor

To account for this phenomenon in a more quantitative way, we must consider the dephasing effect that is associated with a description in terms of hybrid scattering paths, and which is due to the small frequency difference between Raman and Rayleigh waves. With reference to the sketch in Fig. 4, we see that when the reciprocal waves propagate off the same scattering event $\left(r_j - r_{j+1}\right) = -\left(r'_{j+1} - r'_j\right)$ at different frequencies, a phase difference $\Delta\varphi_j = \frac{\left(\omega_j - \omega'_j\right)}{c}\left|r_j - r_{j+1}\right|$ is developed at each scattering step, where c is the speed of light. At the end of whole scattering path, the two waves come out from the scattering system with a total dephasing $\Delta\phi$ given by the sum on all phase steps $\Delta\varphi_j$ and expressed as $\Delta\phi = \left|\sum_j \frac{\left(\omega_j - \omega'_j\right)}{c}\left|r_j - r_{j+1}\right|\right|$. The above argument shows that an interference contribution, and hence a coherent backscattering signal, can be expected for multiple Raman scattering occurring over lights paths in which $\Delta\phi$ remains significantly below π. The presence of a dephasing mechanism in the coherent contribution to multiple Raman scattering is expected to alter significantly the probability of wave diffusion in the disordered material, leading to a modified backscattering cone in a way that is similar to what is observed for multiple scattering from particles subjected to Brownian motion or in the presence of a magnetic field[42]. In general, one can show that dephasing affects the diffusion probability by a global factor $\left\langle e^{i\Delta\phi(t)} \right\rangle$, where $\Delta\phi(t)$ is the phase difference between reciprocal

scattering paths. This phase difference is a random variable whose statistical distribution depends on the specific mechanism at the origin of the dephasing. Normally, the average over this distribution takes the form of a decaying function of time as $\left\langle e^{i\Delta\phi(t)}\right\rangle = e^{-t/\tau_d}$, which provides a physical interpretation for a cut-off time τ_d (corresponding to a cut-off length $L_d = \sqrt{D\tau_d}$) describing the loss of phase coherence. The problem is then reduced to the evaluation of the global factor $\left\langle e^{i\Delta\phi(t)}\right\rangle$, starting from a microscopic description of the dephasing process. We have explicitly calculated this quantity according to the statistical description of coherent Raman backscattering in terms of hybrid Rayleigh-Raman reciprocal paths, as depicted in Fig. 4. This leads to the following expression for the average phase factor: $\left\langle e^{i\Delta\phi(t)}\right\rangle \cong e^{i\langle\Delta\phi\rangle - \langle\delta\Delta\phi^2\rangle/2} = e^{i3D\Delta kt/2\ell_t} e^{-3D\Delta k^2 t/2} = e^{it/\tau_{d1}} e^{-t/\tau_{d2}}$, where $D = \frac{c\ell_t}{3}$ is the diffusion constant. We see that the average phase factor affecting the coherent backscattered intensity is a complex valued function characterized by two different contributions: 1) a fast oscillating term, with a characteristic time (length) period $\tau_{d1} = \frac{2\ell_t}{3D\Delta k}$ set by the average value $\langle\Delta\phi\rangle$ of the dephasing; 2) a slow exponentially decaying term, with a characteristic time (length) constant $\tau_{d2} = \frac{2}{3D\Delta k^2}$ set by the mean square value (variance) $\langle\delta\Delta\phi^2\rangle$ of the dephasing. The combination of these two terms constitutes the coherence function for the RCBS process, which allows us to define two linked dephasing lengths $\ell_{d1} = c\tau_{d1} = \frac{2}{\Delta k}$ and $\ell_{d2} = c\tau_{d2} = \frac{2}{\Delta k^2 \ell_t} = \frac{\ell_{d1}^2}{2\ell_t}$ as the characteristic lengths of the specific dephasing mechanisms. We notice that ℓ_{d2} sets a cut-off for long

scattering paths, for which coherence of the Raman signal is globally lost due to random fluctuations in the phase difference between hybrid paths. On the other hand, ℓ_{d1} represents a sort of phase-matching length, allowing the coherent superposition of reciprocal hybrid paths with both constructive and destructive interference contributions, depending on whether their relative phase difference is close to $2n\pi$ (in-phase paths) or close to $(2n+1)\pi/2$ (out-of-phase paths). For $\ell_{d1} > \ell_t$ (a condition which is easily met in strongly scattering materials) we have $\ell_{d2} >> \ell_{d1}$, and the resulting coherence function is a damped cosine. This peculiar behaviour is in full agreement with the description of the RCBS in terms of hybrid paths, as shown in Fig. 4.

According to this picture, dephasing is expected to have a strong influence not only on the enhancement factor of the observed RCBS cone, but also on its angular shape describing the reduction of the backscattered intensity away from the backscattering direction. According to the general theory of light diffusion in disordered media, to account for this effect in quantitative way we modelled the backscattering intensity in terms of the bistatic coefficient $\gamma = \gamma_c + \gamma_\ell$, where γ_c is the coherent contribution to the scattered intensity, while γ_ℓ is the incoherent term[43]. The effect of dephasing was then explicitly included into γ_c by introducing two additional terms in the extinction coefficient κ_{ext_C}, namely $-i\ell_{d1}$ and ℓ_{d2}^{-1}, which account for the new defined dephasing lengths (see the Supplementary Information Section S1 for details). The best fits to the experimental data in terms of angle-dependent coefficients γ_c and γ_ℓ are indicated in Fig. 2 by the red lines, showing very good agreement in all cases. For each sample, the dephasing length ℓ_{d1} and the theoretical Raman enhancement factor defined as $E_{Raman} = \gamma_c/\gamma_\ell + 1$, with $\gamma_c/\gamma_\ell < 1$, were the only free fitting parameters, while the transport mean free path ℓ_t was fixed to the value

obtained from the corresponding ECBS cones. In particular, we notice the characteristic near flat-top of the Raman backscattering cones (most evident in Fig. 2c). This feature is uniquely determined by the oscillating coherence function entering the γ_c coefficient, and it is intimately linked to the specific dephasing mechanism acting on the hybrid Rayleigh-Raman multiple scattering paths.

Raman Coherent Backscattering and optical absorption

Table 1 summarizes the values of the relevant parameters obtained for sample 1 and sample 2 in different experimental conditions. In particular, we see that the values of ℓ_{d1} determined from the best-fit are of the order of a few microns, while those of ℓ_{d2} are in the range of a few tens of microns, in agreement with the predicted dephasing lenghts calculated from Δk and ℓ_t values in each case. Moreover, since the dephasing affects only the coherent contribution to the bistatic coefficient γ_c, we expect a significant dependence of E_{Raman} on ℓ_{d1} (the dependence on ℓ_{d2} is expected to be much weaker, since typically $\ell_{d2} >> \ell_{d1}$). This is indeed observed from the data reported in Table 1, where we see that lower enhancement factors correspond to lower dephasing lengths. However, a direct relationship between ℓ_{d1} and E_{Raman} cannot be established without considering the effect of the inelastic (absorption) mean free path ℓ_i. This can be readily understood by looking at Fig. 5a, where we report the theoretical dependence of E_{Raman} on both ℓ_{d1} and ℓ_i, normalized to the transport mean free path ℓ_t. Here we see that significant Raman enhancement factors are only possible when $\ell_{d1} > \ell_i$, which implies ℓ_i values of the order of a few microns for typical vibrational frequencies in solid-state materials (we recall that

$\ell_{d1} = \frac{2}{\Delta k} = \frac{2c}{\Delta \omega_{Stokes}}$). The possibility to observe an appreciable coherent backscattering effect for a given Raman active mode in a strongly scattering material is therefore determined, to a large extent, by the presence of absorption in the system. The reason for this counter-intuitive behaviour must be found in the peculiar coherence function governing the interference of multiply scattered Raman waves: indeed, due to its fast oscillations as a function of the scattering path length, the coherence function would rapidly average out to zero in the absence of optical absorption, thus yielding a vanishing contribution to the coherent term of the backscattered intensity with respect to the diffused (incoherent) one. By contrast, the presence of absorption leads to a cut-off of the integral at long scattering paths for both the coherent and diffused contribution, thus making the coherent part of the backscattered intensity emerge over the diffused one. Taking into account the effect of optical absorption, we can finally make a quantitative comparison of our experimental RCBS data with the theoretically predicted values of Raman enhancement in the presence of dephasing. This is reported in Fig. 5a (white dots in the contour plot) and in Fig. 5b, where an almost perfect agreement between theoretical and experimental values of E_{Raman} is found for all measured samples. We notice that while absorption seems to be necessary for the observation of coherence effect in the multiple scattering of spontaneous Raman, the absence of absorption, would strongly increase the interaction length of the light with the matter, paving the way towards interesting nonlinear effects such as stimulated Raman scattering, CARS[44,45] (Coherent Anti-Stokes Raman scattering) and Raman gain from strongly scattering materials[46].

Conclusions

Our findings provide the first experimental evidence, to our knowledge, of the coherent nature of spontaneous Raman scattering revealed on a macroscopic length scale. It manifests through the observation of an enhanced backscattering intensity in the inelastically scattered Raman signal from strongly scattering nanostructured media, in close analogy with the well-known elastic (Rayleigh) coherent backscattering process. This study strongly confirms the robustness of the coherent backscattering phenomenon and, above all, it establishes a new starting point towards unexplored interference phenomena in Raman scattering by disordered media.

METHODS

Sample fabrication. Sample 1: Si NWs were created starting from n-type (P concentration of 10^{16} cm^{-3}) single crystal (111)-oriented Si wafers. The wafers were cut into 1 cm × 1 cm pieces, and then UV oxidized and dipped in 5% HF to obtain clean and oxide-free Si surfaces. Afterwards, a thin gold (Au) layer with a thickness of 2 nm (corresponding to 1×10^{16} Au atoms/cm^2) was deposited on the Si samples at room temperature by electron beam evaporation using high purity (99.9%) gold pellets as a source. Finally, samples were etched at room temperature in an aqueous solution of hydrofluoric acid (HF = 5 M) and hydrogen peroxide (H_2O_2 = 0.44 M) to form Si NWs. After NWs production, Au was completely removed by a KI dip[29]. Following this procedure, we obtained a dense distribution of vertically aligned thin NWs (about 7 nm in diameter) with the same length (2.6 μm) (Fig. 1a, 1b).

Sample 2: Si NWs were synthesized by metal assisted chemical etching using a solution of silver nitrate ($AgNO_3$), HF and H_2O_2 [31,32]. The sample was immersed in an aqueous solution containing

$AgNO_3$ 0.02M as metal precursor and HF 5M as etching agent. The silver salts dissociated realising a precipitation of silver nanoparticles (NPs) that randomly distributed on the silicon surface. Locally, underneath the metal NPs covered region, silicon oxide formed and was subsequently removed by the HF. As a consequence, silver nanoparticles sank into the silicon bulk, leading to the formation of Si NWs. We obtained 8-µm-long NWs with an average diameter of about 100 nm (Fig. 1c, 1d).

Plan view and cross-sectional images of the Si NW arrays were performed using field emission scanning electron microscope (SEM) Zeiss Supra 25.

Coherent backscattering. Coherent backscattering in the range (-90°, 90°) for both Rayleigh and Raman wavelengths was measured with a homemade goniometer fibre-coupled to a liquid-nitrogen-cooled Si-CCD (Spec 400 BR, Princeton Instruments) with an angular resolution of about 0.1° (set by the collection optics). Optical excitation was provided by a laser beam focused to a 1-mm diameter spot onto the sample surface (continuous-wave solid state lasers at 532 nm and 488 nm, and a diode laser at 785 nm). To obtain the coherent contribution to the scattering intensity we used a circular polarized light configuration, with an analyzer in front of the detector, to collect the helicity conserving channel which excludes single scattering events and reflections from the optical set-up. The incoherent contribution was obtained by measuring the linear polarization non-conserving channels as average for *s* and *p* polarizations. The coherent contribution was then scaled such that its intensity coincides with the incoherent contribution at large angles (larger than 60°). The normalized backscattering cones were finally obtained by dividing the helicity conserving channel by the diffuse background. Note that all datasets were acquired by positioning the sample on a rotating mount in order to ensure efficient configuration averaging of the scattering paths and eliminate laser speckles.

The error bars shown for ECBS and RCBS cones (Fig. 1.e,f and Fig. 2) and for the angular dependences of the Raman scattered light and PL emission (Fig. 3b) are related to the points at the exact backscattering angle; the error bar of the spectrum shown in Fig. 3a is representative of the signal noise.

The data that support the plots within this paper and other findings of this study are available from the corresponding authors upon reasonable request.

ACKNOWLEDGMENTS

We wish to thank Ad Lagendijk, N. Micali, F. Aliotta and S. Trusso for helpful and stimulating discussions.

D.S.W. acknowledges support by the European Research Council under the European Union's Seventh Framework Programme (FP7/2007-2013) / ERC grant agreement n° [291349].

F.P. acknowledges partial support by the European Commission and MIUR through the projects PON02_00355_3391233 named Energetic and PONa3_00136 named BRIT.

AUTHOR CONTRIBUTIONS:

B.F. proposed the experiments and initiated the project; B.F. and M.G. conceived the idea of Coherent Raman Backscattering. A.I. realized the samples and performed the structural characterization, with contributions from M.J.L.F., C.D. and P.M.; S.P. and S.D.S. realized the experimental setup and performed the experiments under supervision of M.G., with contributions from C.D. and B.F; B.F. and C.D. performed the data analysis, with contribution from M.A.I, R.S. and M.G.; D.S.W. developed the theoretical formalism of multiple Raman scattering; M.G.

and S.D.S. developed the theoretical model of dephasing; B.F. and M.G. interpreted the data with inputs from D.S.W; B.F. and M.G. co-wrote the paper with contributions from A.I. and F.P.; B.F., M.G. and F.P. coordinated the project. All the authors contributed to the general discussion and to the manuscript revision.

Si NW Sample	Fixed parameters ECBS and RCBS				Fitting parameter ECBS		Fitting Parameters RCBS (ℓ_t fixed)		Evaluated parameter
	$\lambda_{exc}(\mu m)$	n_{eff}	$a = z_0/\ell_t$	$\ell_i(\mu m)$	$\ell_t(\mu m)$	L_{eff}/ℓ_t	E_{Raman}	$\ell_{d1}(\mu m)$	$\ell_{d2}=\ell_{d1}^2/2\ell_t(\mu m)$
sample 1	0.488	1.40 ± 0.14	1.6	4.5	0.15 ± 0.02	18 ± 6	1.75 ± 0.08	3.9 ± 0.4	50 ± 10
sample 1	0.532	1.36 ± 0.14	1.5	8.1	0.17 ± 0.02	17 ± 5	1.62 ± 0.08	3.4 ± 0.3	34 ± 7
sample 1 (with silicone oil)	0.532	1.72 ± 0.17	2.3	8.1	0.22 ±0.02	9 ± 0.5	1.45 ± 0.07	2.9 ± 0.3	19 ± 4
sample 1	0.785	1.32 ± 0.13	1.4	86.5	0.19 ± 0.02	13 ± 0.5	1.44 ± 0.07	5.6 ± 0.5	81 ± 13
sample 2	0.532	1.73 ± 0.25	2.3	3.8	0.48 ± 0.02	5 ± 0.2	1.28 ± 0.07	2 ± 0.4	4 ± 1.6

Table 1. List of samples and fitting parameters for the ECBS and RCBS cones.

We fixed the excitation wavelength λ_{exc}, the refractive index n_{eff}, the parameter a (taking into account the internal reflection at the boundaries) and the inelastic (absorption) mean free path ℓ_i. We estimated the values of n_{eff} and ℓ_i by morphological analysis (SEM) and EDX spectroscopy, for which we obtained a volume fraction of 10 ± 2 % of silicon and 9 ± 2 % of SiO_2 for sample 1 (diameter 7±2 nm, length 2.6 μm) and 22 ± 4 % of silicon and 3 ± 1 % of SiO_2 for sample 2 (diameter 100±20 nm, length 8 μm). We fit the Rayleigh cones by using the transport mean free path ℓ_t and the effective thickness L_{eff} as free parameters (see Supplementary Information Section S1 for details). We fit the RCBS cones by using the dephasing length ℓ_{d1} and the theoretical Raman enhancement E_{Raman} as fitting parameters. The transport mean free path ℓ_t is fixed at the values obtained by ECBS fits.

Figure legends

Figure 1. Structural characterization and ECBS cones for silicon nanowire materials. In **a** and **b** plan view and cross section scanning electron microscopy images of the Si NW sample 1 are shown, respectively. The plan view and cross section SEM images of the Si NW sample 2 are shown in **c** and **d** panels. The inset in the plan view image **c** is a zoom to a higher magnification in order to compare the two materials at the same scale. **e,f.** Coherent backscattering cones after normalization to the diffusive background signals referred to Si NW sample 1 and 2 (**e** and **f** respectively). The red solid lines are best fitting curves obtained with the finite slab model (see Supplementary Information Section S1). In the inset, a schematic of the Elastic (Rayleigh) Coherent Backscattering principle is shown. ψ is the angle formed between the incoming and the outgoing light wavevectors, θ is the incidence angle; it should be noted that the backscattering direction ($\psi=\theta$) is in general different from the direction of specular reflection; the two coincide only at normal incidence. The error bars are indicated as a legend in the graph.

Figure 2. Coherent backscattering cones for Rayleigh and Raman radiations. Coherent Backscattering cones for Rayleigh (blue dots) and Raman (dark yellow dots) scattering in sample 1 at different excitation wavelength: (**a**) 488 nm, (**b**) 532 nm, (**c**) 785 nm and (**d**) 532 nm with silicone oil filling. The solid red lines represent best fitting curves obtained with a finite slab model for the Raman case (see Supplementary Information Section S1 for details). The error bars are indicated as a legend in the graph.

Figure 3. Comparison between the angular dependence of the Raman scattered light and that of the photoluminescence emission.

a. Raman spectrum of Si NW sample 1 obtained in the helicity conserving channel (CC) configuration (see Methods) by exciting with a laser line at 532 nm. The integrated Raman intensity of the first order scattering Si Raman peak (**a.** light blue area) and the PL background around the Raman peak (**a.** pink area), evaluated on the same narrow wavelength range (here expressed in Raman shift), were plotted as a function of the scattering angle in **b**. The PL curve shape (**b.** pink dots) follows a perfect cosine law, deviating from the Raman curve (**b.** light blue dots) that displays coherent enhancement around the backscattering direction. The intensities are scaled such that the PL emission at the exact backscattering direction is 1. The error bars are indicated as a legend in the graph.

Figure 4. Coherent Raman Backscattering process: illustration of basic concepts.

a. Schematic picture of light transport in mixed Rayleigh-Raman paths. In the inset a zoom on the depicted Raman scattering at $\boldsymbol{R}$ is shown: in the "direct" Rayleigh-Raman scattering path **(b)**, a photon of frequency ω_i and polarization $\boldsymbol{e}_i$ is Raman scattered by a Si nanowire with a cross-section σ_D, giving rise to a photon of frequency ω_s and polarization $\boldsymbol{e}_s$. In the "reverse" path **(c)**, the Rayleigh and Raman photons are exchanged and propagation directions reversed: a photon of frequency ω_i and polarization $\boldsymbol{e}_i' \equiv \boldsymbol{e}_s$ is Raman scattered by the *same* Si nanowire with a cross-section σ_R, giving rise to a photon of frequency ω_s and polarization $\boldsymbol{e}_s' \equiv \boldsymbol{e}_i$. **d.** Assuming $\omega_i \approx \omega_s$, the Raman tensor $R(\omega_i, \omega_s)$ is symmetric with respect to exchange of $\boldsymbol{e}_i$ and $\boldsymbol{e}_s$, yielding $\sigma_D = \sigma_R$.

The incident and scattered light wavevectors form the angle θ. Since they have the same modules ($\boldsymbol{k}_i \approx \boldsymbol{k}_s$ and $\boldsymbol{k}'_i \approx \boldsymbol{k}'_s$), the phonon wavevector $\boldsymbol{q}$ is the same for both scattering paths.

Figure 5. Enhancement of Raman Coherent backscattering cones: comparison between experimental data and theoretical model.

a. Colour scaled contour plot representation of the theoretical coherent Raman enhancement (at $\psi=0$) as a function of the dephasing length (x axis) and the inelastic mean free path (y-axis), both expressed in units of the transport mean free path (the axes are represented in logarithmic scale). The E_{Raman} values obtained by the fitting procedures for all the experimental data sets are superimposed to the contour plot. **b.** Theoretical trends of coherent Raman enhancement are plotted as a function of the dephasing length (in units of ℓ_t) for different inelastic mean free paths. The dots and the corresponding error bars in the graph represent the experimental data for the entire set of measurements: sample 1 excited at 488, 532 and 785 nm (blue, green and red dots, respectively), sample 1 filled with silicone oil and excited at 532 nm (green square) and sample 2 excited at 532 nm (black dot).

REFERENCES

1. Sheng, P. *Introduction to Wave Scattering, Localization and Mesoscopic Phenomena* 2nd edn (Springer, 2010).
2. John, S. Localization and absorption of waves in a weakly dissipative disordered medium. *Phys. Rev. B* **31**, 304- 309 (1985)**.**
3. Wiersma, D.S., Bartolini, P., Lagendijk, A. & Righini, R. Localization of light in a disordered medium. *Nature* **390**, 671-673 (1997).
4. Segev, M., Silberberg, Y., Christodoulides, D.M. Anderson localization of light. *Nat. Photon.* **7**, 197-204 (2013).
5. Wiersma, D.S. The physics and applications of random lasers. *Nat. Physics* **4**, 359-367 (2008).
6. Wiersma, D.S., Van Albada, M.P. & Lagendijk, A. Random laser? *Nature* **373**, 203-204 (1995).
7. Wiersma, D.S. Disordered Photonics. *Nat. Photon.* **7**, 188-196 (2013).
8. Kuga, Y & Ishimaru, A. Retroreflectance from a dense distribution of spherical particles. *J. Opt.. Soc. Am. A,* **8**, 831-835 (1984).
9. Van Albada, M.P. & Lagendijk, A. Observation of Weak Localization of Light in a Random Medium. *Phys. Rev. Lett.* **55**, 2692-2695(1985).
10. Wolf, P.E. & Maret, G. Weak Localization and Coherent Backscattering of Photons in Disordered Media. *Phys. Rev. Lett.* **55**, 2696-2698 (1985).
11. Gantmakher, V.F. Electrons and Disorder in Solids. *International Series of Monographs on Physics* 130, Oxford University Press (2005).

12. Muskens, O.L. & Lagendijk, A**.** Broadband enhanced backscattering spectroscopy of strongly scattering media, *Opt. Expr.* **16** , 1222-1231 (2008).

13. Labeyrie, G., de Tomasi, F., Bnard, J.-C. , Müller, C. A. , Miniatura, C., & Kaiser R. Coherent Backscattering of Light by Cold Atoms. *Phys. Rev. Lett.* **83**, 5266 (1999).

14. Labeyrie, G., Muller, C.A., Wiersma, D.S., Miniatura, C. and Kaiser, R. Observation of coherent backscattering of light by cold atoms. *J. Opt. B.: Quantum Semiclass. Opt.* **2**, 672-685 (2000).

15. Sapienza, R., Mujumdar, S., Cheung, C., Yodh, A.G. & Wiersma, D. Anisotropic Weak Localization of Light**.** *Phys. Rev. Lett.* **92**, 033903-1 -033903-4 (2004).

16. Derode, A., Mamou, V., Padilla, F., Jenson, F., Laugier, P. Dynamic coherent backscattering in a heterogeneous absorbing medium: Application to human trabecular bone characterization. *Appl. Phys. Lett.* **87**, 114101-1 - 114101-3 (2005).

17. Yoo, K. M., Tang, G. C. & Alfano, R. R. Coherent backscattering of light from biological tissues. *Appl. Opt*. **29,** 3237–3239 (1990).

18. Muskens, O.L., Venn, P., Van de Beek, T. &Wellens, T. Partial Nonlinear Reciprocity Breaking through Ultrafast Dynamics in a Random Photonic Medium. *Phys. Rev. Lett.* **108**, 223906-1 - 223906-5 (2012).

19. Bromberg, Y., Redding, B., Popoff, S.M. & Cao, H. Control of coherent backscattering by breaking optical reciprocity. *Phys. Rev. A* **93**, 023826-1 - 023826-6 (2016).

20. Chanelière, T., Wilkowski, D., Bidel, Y., Kaiser, R. and Miniatura, C. Saturation-induced coherence loss in coherent backscattering of light. *Phys. Rev. E* **70**, 036602-1 - 036602-4 (2004).

21. Balik, S. *et al.* Strong-field coherent backscattering of light in ultracold atomic ^{85}Rb. *J. Mod. Opt.* **52**, 2269-2278 (2005).

22. Labeyrie, G., Delande, D., Muller, C.A., Miniatura, C. & Kaiser, R. Coherent backscattering of light by cold atoms: Theory meets experiment. *Europhys. Lett.* **61**, 327-333 (2003).

23. Otto, A. Theory of first layer and single molecule surface enhanced Raman scattering. *Phys. Stat. Sol. A* **188**, 1455–1470 (2001).

24. Beams, R., Cançado, L.G., Oh, S.H., Jorio, A. & Novotny, L. Spatial Coherence in Near-Field Raman Scattering, *Phys. Rev. Lett.* **113**, 186101-1 - 186101-5 (2014).

25. Waldermann, F.C. *et al.* Measuring phonon dephasing with ultrafast pulses using Raman spectral interference. *Phys. Rev. B* **78**, 155201-1 - 155201-6 (2008).

26. Kupriyanov, D.V., Sokolov, I.M. and Havey, M.D. Antilocalization in coherent backscattering of light in a multi-resonance atomic system. *Opt. Commun.* **243**, 165-173 (2004).

27. Kupriyanov, D.V., Larionov, N.V., Sokolov, I.M. and Havey, M.D. Destructive Interference in Coherent Backscattering of Light by an Ensemble of Cold Atoms. *Opt. Spectrosc.* **99**, 380-385 (2005).

28. Priolo, F., Gregorkiewicz, T., Galli, M. & Krauss, T. F. Silicon nanostructures for photonics and photovoltaics. *Nat. Nanotech.* **9**, 19–32 (2014).

29. Irrera, A. *et al.* Quantum confinement and electroluminescence in ultrathin silicon nanowires fabricated by a maskless etching technique. *Nanotechnology* **23**, 075204-075210 (2012).

30. Fazio, B. *et al.* Strongly enhanced light trapping in a two-dimensional silicon nanowire random fractal array. *Light Sci. Appl.* **5**, e16062, doi:10.1038/lsa.2016.62 (2016).
31. Peng, K. Q., Wu, Y. , Fang, H., Zhong, X. , Xu Y. & Zhu J., Uniform, Axial-Orientation Alignment of One□Dimensional Single-Crystal Silicon Nanostructure Arrays, *Angew. Chem. Int. Edn* **44**, 2737 - 2742 (2005).
32. Peng, K. Q., Yan, Y., Gao S. P. & J. Zhu, Dendrite-Assisted Growth of Silicon Nanowires in Electroless Metal Deposition, *Adv. Funct. Mater*. **13**, 127-132 (2003).
33. Akkermans, E., Wolf, P.E. , Maynard R. Coherent Backscattering of Light by Disordered Media: Analysis of the Peak Line Shape. *Phys. Rev. Lett*. **56**, 1471-1474 (1986).
34. Akkermans, E., Wolf, P.E., Maynard, R. , Maret, G. Theoretical study of the coherent backscattering of light by disordered media. *J. Phys. France* **49**, 77-98 (1988).
35. Van der Mark, M.B., Van Albada, M.P. & Lagendijk, A. Light scattering in strongly scattering media: Multiple scattering and weak localization. *Phys. Rev. B* **37,** 3575-3592 (1988).
36. Loudon, R. Theory of first-order Raman effect in crystals. *Proceeding of the royal Society of London. Series A. Mathematical and Physical Sciences.* **275**, 218-232 (1963).
37. Yu, P.Y. & Cardona, *M., Fundamentals of Semiconductors, 4th edition* (Springer Heidelberg Dordrecht, New York, 2010).
38. Loudon, R. , The Raman effect in crystals, *Advances in Physics*, **13**, 52, 423-482 (1964).
39. The aforementioned symmetry property holds whatever the crystal symmetry; however, the further requirement that the Raman tensor should be invariant under the symmetry operations of the crystal imposes further limitations. In the general case the Raman tensor

529 is strictly symmetric for all the crystals having inversion symmetry, as the case of most
530 semiconductors and of silicon in particular.
531 40. Letcher, J.L., Kang, K., Cahil, D.G., Diott, D.D. Effects of high carrier densities on
532 phonon and carrier lifetimes in Si by time-resolved anti-Stokes Raman scattering. *Appl.*
533 *Phys. Lett.*, **90**, 252104-1–252104-3 (2007).
534 41. Henry, A.S. & Chen, G. Spectral Phonon Transport Properties of Silicon Based on
535 Molecular Dynamics Simulations and Lattice Dynamics. *Journal of Computational and*
536 *Theoretical Nanoscience*, **5**, 1-12 (2008).
537 42. Akkermans, E. & Montambaux, G. *Mesoscopic Physics of Electrons and Photons*.
538 (Cambridge University Press, Cambridge, 2007).
539 43. Wiersma, D.S. Light in strongly scattering and amplifying random media. *PhD thesis.*
540 *University of Amsterdam*, 144 (1995).
541 44. Baibarac, M., Baltog, I. , Lefrant S. Abnormal anti-Stokes Raman emission as single
542 beam coherent anti-Stokes Raman scattering like process in $LiNbO_3$ and CdS powder. *J.*
543 *Appl. Phys.* **110**, 053106-1 - 053106-6 (2011).
544 45. Raymond Ooi, C. H. *et al.* Theory of femtosecond coherent anti-Stokes Raman
545 backscattering enhanced by quantum coherence for standoff detection of bacterial spores.
546 *Phys. Rev.* A **72**, 023807-1-023807-13 (2005).
547 46. Hokr, B.H. *et al.* Bright emission from a random Raman laser. *Nat. Commun*. **5**, 4356
548 (2014).
549