Sagnac interferometer for photothermal deflection spectroscopy

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Photothermal deflection spectroscopy is combined with a Sagnac interferometer to enhance the sensitivity of the absorption measurement by converting the photothermal beam deflection effect into the light intensity change by the interference effect. Because of stable light interference due to the common path, the signal intensity can be amplified without increasing the noise by extending the optical path length between a sample and a photodetector. The sensitivity is further improved by the use of focusing optics and double-pass geometry. This makes photothermal deflection spectroscopy applicable to any kind of material in the whole visible region with a xenon lamp for excitation and water or air as a deflection medium.

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Photothermal deflection spectroscopy (PDS) [1] is one of the most successful methods among many variations of photothermal spectroscopic methods [2–7]. In conventional PDS, a sample is immersed in a deflection medium that has a large temperature coefficient of the refractive index, dn/dT. The sample is photoexcited with pump light to emit heat, generating a gradient of the refractive index dn/dz in the medium close to the sample surface. A probe laser beam incident in the medium is deflected by the refractive index gradient and the resulting lateral shift of the beam is detected with a position sensitive detector (PSD). The dependence of the size of the shift on the wavelength of the pump light gives a photothermal spectrum of the sample, equivalent to the absorption spectrum on appropriate conditions.

The conventional PDS has, however, plenty of room for improvement. First, when a laser light source is used for the pump, an extremely high sensitivity is available due to the highly focused intensity, but the wavelength range is restricted within a generally narrow tuning range of the laser. Second, as the deflection medium, carbon tetrachloride (CCl_4) is most frequently used [8] because it has a large dn/dT and is chemically inactive. However, a variety of samples is restricted because nonpolar organic material is dissolved in CCl_4, for example.

In this Letter, we have developed a Sagnac interferometer for PDS (SPDS). Recently, ultrasensitive beam deflection measurement with a Sagnac interferometer was reported based on weak measurement [9,10]. Although we do not use their weak measurement protocol, the method has a distinct advantage over the conventional PDS as follows: An extremely small deflection angle is sensitively detected as the intensity change of the interfered light from the Sagnac interferometer, and the signal magnitude is intentionally amplified with the length of the interferometer arm without increasing the noise that originates from fluctuation in the optical elements. This enabled us to obtain photothermal spectra in the full visible spectral range with a white-light lamp source as the pump and with air as the deflection medium.

Figure 1 shows the schematic of the experimental setup for SPDS. A Sagnac interferometer was illuminated by a probe He–Ne laser (Model 32734, Research Electro-Optics) at 633 nm with 3 mW output power, through an optical isolator, a pinhole of 200 μm diameter, and a polarizer. The laser beam was divided into two with a beam splitter, which is the input port as well as the output port of the interferometer. The two beams were delivered into clockwise (CW) and counterclockwise (CCW) propagating arms. The two arms make a common path assuring the stability against fluctuation in the path length difference, suited to measure small imbalance between them induced by an external perturbation [11–13]. The two beams were recombined at the beam splitter to be detected with a photodiode (S1336-BQ8, Hamamatsu) placed at the dark port. Here, the beams interfere destructively to yield zero intensity if they are completely superposed in space due to π phase difference brought by the beam splitter.

A measured sample immersed in an appropriate deflection medium (water or CCl_4 in a glass cell, or air) was placed at an asymmetrical position in the common path. A monochromated Xe lamp (150 W, L2274, Hamamatsu) with 12 nm bandwidth through an $F = 150$ mm monochromator (Acton SP-150) with a grating of 1200 gr/500 nm was used for the pump light. It was intensity-modulated at $f = 20$ to 50 Hz with an optical chopper, and focused with an $F = 17$ mm aspherical lens into the sample from above. The excitation power and intensity were respectively 6.5 μW and 650 μW/cm^2. The sample was so positioned with translational stages that the probe beams passed by immediately above the pump-focused spot on the sample. If the pump is absorbed, all the relaxation paths except for radiative relaxation contribute to heat generation to induce a temperature gradient dT/dz in the deflection medium close to the sample. The dT/dz is transformed into the refractive index gradient dn/dz in the medium to deflect the probe beam at a deflection angle θ. The detection principle is explained in Fig. 2. Since the light traveling distance D from the sample to the photodiode is different between the CW and CCW beams, the lateral

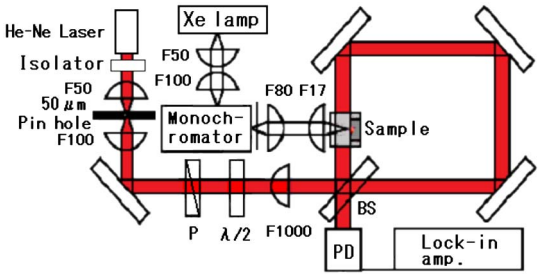

Fig. 1. (Color online) Experimental setup for a Sagnac interferometer for photothermal deflection spectroscopy (SPDS). P, polarizer; $\lambda/2$, half wave plate; BS, beam splitter; PD, photodiode; F50, lens with 50 mm focal length.

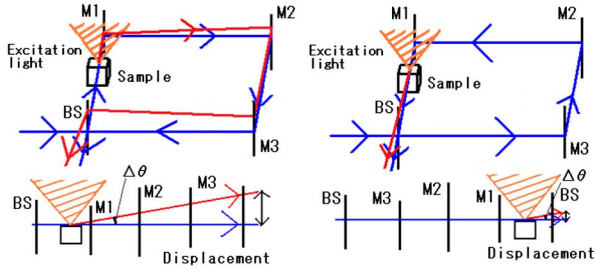

Fig. 2. (Color online) Imbalance in the lateral shift of the beams on the detector surface between the two (CW and CCW) arms of the interferometer.

displacement $D \tan\theta$ of the beams at the photodiode is different between the beams even for the same deflection angle at the sample position. As a result, destructive interference is partially broken to increase the light intensity at the detector. To be precise, the two beams were slightly displaced initially because the light intensity change is larger at a displaced position than at the completely overlapped position as explained below. The light intensity change, which was synchronous with the modulation frequency f of the pump light, was detected with a lock-in amplifier (Model 7265, Signal Recovery). The beam diameter was about 1.4 mm at the detector whose size was 5 mm square. The PD spectrum of the sample was given by the light intensity change as a function of the pump wavelength.

The light intensity change $\Delta I(x)$ as a function of the lateral displacement x of the two beams was calculated, as shown in Fig. 3(a). The beam pattern was assumed to have an electric field amplitude $E(x',y') \propto \exp[-(x'^2 + y'^2)/a^2]$ with the beam radius of a. The interfered intensity is given by $I(x) \propto \int dx'dy'S(x',y',x)$ with $S(x',y',x) = [E(x'-x/2,y') - E(x'+x/2,y')]^2$. The intensity $I(x)$ is a monotonously increasing function with x having an inflection point at a slightly displaced position ($x = 0.55$ mm). Since the signal detected is the small intensity change induced by a small beam displacement, the signal intensity is proportional to the first derivative of the function $I(x)$. Therefore the interferometric measurement is most sensitive when the beam is initially displaced to the position at the inflection point. Figure 3(b) shows the result of calculation in the weak measurement with a PSD as a detector. The amplified displacement R is obtained as the peak separation of the interfered

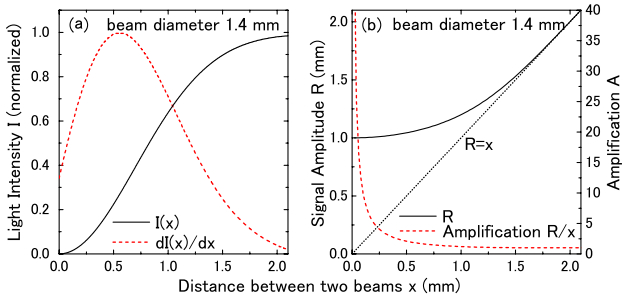

Fig. 3. (Color online) (a) Solid curve $I(x)$: calculated intensity I of the interfered two probe beams as a function of the distance x (the lateral shift) between the central positions of the two beams. Dashed curve $\Delta I(x)$: intensity change, which is proportional to the first derivative of $I(x)$. (b) Amplified displacement signal calculated with the weak measurement protocol. See the text for details.

intensity $S(x',y',x)$ along x' by solving numerically the equation of $\frac{dS(x',y',x)}{dx'} = 0$. In this method, the gain in the amplification A is compensated for the reduction in the interfered light intensity $I(x)$. For example, $A = 50$ at $x = 0.01$ mm. In photothermal deflection spectra, however, $\Delta R(= \frac{dR}{dx}\Delta x)$ is detected as the beam deflection varies continuously from x to $x + \Delta x$. Figure 3(b) shows $\frac{dR}{dx} = 0$ for $x = 0$ although $A = \infty$, and $\frac{dR}{dx}$ monotonously increases to converge to its largest value of unity as x is increased over the beam diameter. Therefore, the weak measurement is not suited for detecting a continuously varying deflection. This is the reason why we did not adopt the weak measurement method.

In conventional PDS, the deflected beam position is detected with a PSD that is placed at an appropriate distance D from the sample. In this case, the signal intensity (lateral beam displacement $D \tan\theta$) is amplified as D is increased, but the noise is also amplified with D because of fluctuation of the optical elements or the laser beam. In SPDS, on the other hand, the beam deflection was detected as the intensity change of the interfered beams. Since the Sagnac interferometer stabilizes the beam overlap against the fluctuation, the signal is amplified with D without the noise amplification. Therefore, the signal-to-noise ratio (S/N) can be improved by simply increasing the arm lengths of the interferometer. This is demonstrated in Fig. 4. Strictly,

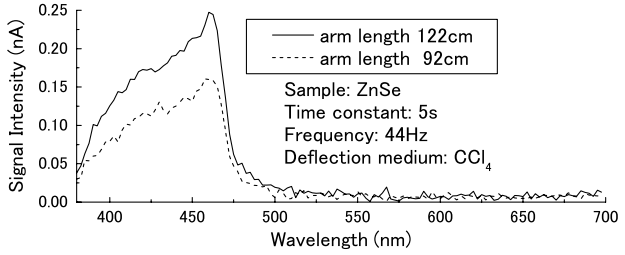

Fig. 4. The arm length dependence of SPDS spectra (not normalized with the pump light spectrum) of ZnSe immersed in CCl_4 detected at $f = 44$ Hz without focusing the probe light at the sample. The arm length is defined by the path length (from the sample to the photodiode) difference between the CW and CCW paths.

Table 1. TDL and dn/dT for Typical Deflection Media

Deflection medium	TDL (mm) at $f = 15$ Hz	dn/dT (K^{-1})
Air	0.62703	-9.73381×10^{-7}
H_2O	0.053372	-7.7147×10^{-5}
CCl_4	0.15779	-6.60082×10^{-4}

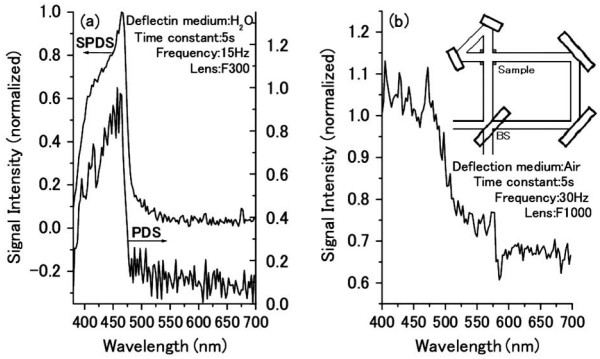

Fig. 5. (a) Comparison between PDS and SPDS spectra for ZnSe with water as deflection medium; (b) SPDS spectrum for Ag_3PO_4 powder with air as deflection medium, normalized with the lamp spectrum. The probe was focused with an $F = 1000$ mm lens and double beam-pass geometry was employed. The photothermal spectrum of charcoal was used as the lamp spectrum for normalization. Around 575 nm, a structure originating from the spectral response in the monochromator is not completely compensated for by normalization.

a Sagnac interferometer is robust only against parallel movement of the optical elements and laser beams. The stabilization mechanism does not work against rotational motion of the optical elements and the pointing instability of the laser. The result in Fig. 4 indicates that the latter fluctuation has a minor contribution to the whole fluctuation mechanism. As a result, there is a significant improvement in S/N for SPDS compared with that for PDS, as shown in Fig. 5(a).

Thermal diffusion length (TDL) is given by spatial extension of a temperature gradient dT/dz from the sample surface. TDL is specific to the medium surrounding the irradiated sample. The deflection angle is larger for the larger dn/dT, because the larger dn/dz results from dT/dz within the TDL. The deflection angle is modulated synchronously with the temperature modulation induced by the modulated pump light. The temperature modulation is conveyed by the temperature wave, whose amplitude decays to $1/e$ as it is propagated over the TDL. It is therefore desirable that the probe beam diameter is smaller than the TDL of the deflection medium. In Table 1, TDL and dn/dT are listed for three representative deflection media.

In order to satisfy this condition for improved sensitivity, a focusing lens of $F = 1000$ mm was placed before the input port to reduce the CW probe beam diameter into ca. 630 μm immediately above the pump-focused spot on the sample. The experimental result for Ag_3PO_4 powder [14] with air as a deflection medium is shown in Fig. 5(b). In this measurement, the sensitivity was further improved by employing double beam-pass geometry as in Fig. 5(b). From the signal intensity, the measurable limit of temperature change in air on the sample surface is estimated to be 10^{-5} K, 1 order of magnitude better than that for the original report on PDS [1].

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