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New photothermal deflection technique to discriminate between heating and cooling

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ABSTRACT

Photothermal deflection spectroscopy (PDS) is a highly sensitive and precise technique that is used to measure the optical absorption and thermal characteristics of a sample. While most applications of PDS utilize a heating beam, laser cooling of solids, or optical refrigeration as it is sometimes called, use this technique to determine if a laser is cooling or heating a sample. Current PDS methods for laser cooling require multiple laser wavelengths in both the Stokes and anti-Stokes region to ensure that cooling is occurring. This can cause problems if lasers must be changed or no lasers in the desired wavelength are available. Herein, we present a photothermal deflection technique that uses the deflection of the probe laser to determine if microcooling is occurring inside a sample.

Photothermal deflection spectroscopy (PDS) is one of the most sensitive methods of molecular absorption spectroscopy. It belongs to a class of photothermal spectroscopy that includes photoacoustic and thermal lensing. These methods rely on the absorption of electromagnetic radiation by a medium, which leads to some or all of this energy being converted to thermal energy through nonradiative processes. For PDS, the source of the electromagnetic radiation is supplied by a modulated laser beam (pump beam). This beam produces modulated thermal gradients, which is detected by a passing probe beam (usually a stable HeNe laser) located either inside the transparent media or adjacent to the medium. These thermal gradients produce changes of the index of refraction, which cause the probe beam to be spatially deflected. The amplitude of this deflection is determined using a position sensitive detector, which can be used to determine the optical absorption of the sample [1–4].

Typically, there are two types of PDS experiments: collinear or transverse. Transverse measurements are typically performed on opaque solids. Here, the probe beam typically propagates through a transparent medium, which is in contact with the surface of the solid that is being irradiated by the pump beam at the normal incidence [2]. For collinear PDS, the two beams are aligned such that they are nearly parallel and closely overlap within the sample. This geometry is advantageous because the beams have a larger interaction distance, which produces a larger deflection signal [2].

Today, PDS is widely used owing to its high spectral, spatial, and temporal resolution, high sensitivity, as well as it being a noncontact, nondestructive method. As such, this technique is routinely applied to measure the optical, thermal, and thermo-elastic materials properties of materials and thin films [5–7]. PDS was first used by Boccara et al. to measure small optical absorptions in solids [8]. Since then there have been many PDS theoretical models and setups have been proposed to precisely determine the optical characteristics of materials. For example, Mandelis et al. proposed a 1D model to determine the optical absorption coefficient of opaque samples using the amplitude and phase of the photothermal deflection, Yacoubi et al. showed that the PDS measurements of the absorption coefficient and thermal conductivity of stacked heterostructures matched that of spectroscopic ellipsometry [9], and Skumanich used PDS to measure the optical absorption of C_{60} thin films down to 0.4 eV [10]. The results of these and many other researchers have shown that PDS is capable of measuring smaller optical absorptions more precisely than conventional optical transmission spectroscopy techniques [11].

Later, Saadallah et al. developed a model from carbon black film to determine the thermal diffusivity of paraffin oils using the PDS deflection angle [12]. Salazar et al. developed a complete theoretical model for PDS to determine the thermal diffusivity of solids [13]. Similarly, Fournier et al. developed a theoretical model to investigate optically thin and thick semiconductors [14]. Gharib et al. took it a step further and used PDS to measure the thermal diffusivity and conductivity simultaneously by depositing a layer of graphite on top of the film samples so that the measured signal is sensitive to both the thermal diffusivity and conductivity [15].

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One of the newer and more interesting applications of PDS is depth profiling. Since the thermal diffusion length is dependent upon the modulation frequency, the thermal wave penetration of the pump beam can be controlled by the modulation frequency. By simply changing the modulation of the pump beam, one can scan a thermally thin sample through its depth to measure its thermal properties [11]. Faubel et al. developed a photothermal double beam laser scanning system for scanning an artificial membrane that can be used for measuring thermal properties of a sample's surface as well as the deeper layers without having to move the sample [16]. Similarly, Gaiduk et al. used PDS as a thermal imager to localize single viruses. In fact, they were able to determine that the optical absorption cross section for single chromophores was 4 Å^2 [17].

As one can see, PDS is a very powerful technique that has a wide range of applications especially in the thermal sciences. While most applications have been devoted to studying the heating effects, researchers looking at optical refrigeration or laser cooling of solids have begun using this technique to determine cooling. Laser cooling of solids uses anti-Stokes emission to annihilate phonons from materials, which in turn cools materials. It can be used to achieve an all-solid-state cryocooler that is compact, contains no moving parts, has a high reliability, and does not require the use of cryogenic fluids [18–23]. In 2002, Epstein and his team was the first group to achieve laser cooling of solids using a ZBLANP glass sample [24]. Later in 2010, cryogenic temperature was first attained using a $LiYF_4:Yb^{3+}$ crystal [20]. To date, laser cooling has been mostly limited to glasses and crystals doped with rare-earth elements [23]. However, research has expanded to semiconductors owing to their more efficient pump light absorption, potential for lower temperatures, and the ability to directly integrate the material into electronic and photonic devices. Recently, Zhang et al. demonstrated 40 K of cooling of CdS nanoribbons [25], while the authors measured a small 2.3 °C cooling of CdSe/ZnS QDs [26].

The transition from rare-earth crystals to semiconductors has meant going from millimeter sized samples to the nanoscale to reduce the probability of reabsorption of the emitted photons. As such, tedious noncontact temperature methods must be employed to accurately measure the temperature of the QD(s). As such, PDS is typically used to determine the optimum wavelength for cooling as well as determine if microscopic cooling is occurring within a sample. If microscopic cooling occurs, then there is the potential for bulk cooling of the sample.

Unfortunately, current PDS methods for laser cooling of solids requires multiple pump laser wavelengths, i.e., wavelengths far in the Stokes region to guarantee heating as well as wavelengths in the anti-Stokes regions beyond the mean effective wavelength for possible cooling. The phase change produced by the cooling and heating beams is recorded on an oscilloscope to show cooling, i.e., the Stokes or heating beam is deflected one way, while the anti-Stokes or cooling beam is deflected in the opposite direction. Herein, we propose a new photothermal deflection method that does not require the use of multiple wavelengths to determine cooling. Instead, only the deflection of the probe beam with respect to the pump beam is required to determine if heating or cooling is occurring inside a sample.

1. Methods

CdSe/ZnS QDs (QSP-630) were purchased from Ocean NanoTech. These QDs have an emission spectrum centered at 630 nm and an external quantum efficiency of 80% according to the manufacturer. A 3 mL solution containing 5 mg/mL of CdSe/ZnS to toluene (Fisher T324 ACS grade) was mixed inside a UV fused quartz cuvette with an airtight stopper (Thorlabs CV10Q3500FS). Coherent OBIS LX lasers were used for the anti-Stokes wavelengths, while a Thorlabs L5209120 laser diode was used for the Stokes wavelength.

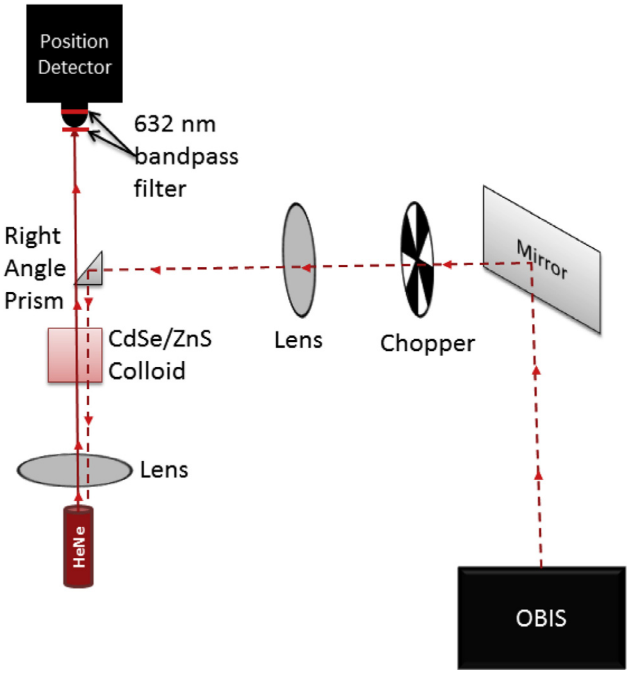

Fig. 1. Diagram showing the photothermal deflection setup.

Photothermal deflection was employed to measure the local temperature gradients induced by the laser inside the colloid. Fig. 1 shows a diagram of the photothermal deflection setup. A mode stabilized Spectra Physics Model 117A HeNe laser probe beam was aligned such that the beam passes through the CdSe/ZnS colloid and is in the center of a position sensitive detector. The OBIS (637, 640, 647, and 660 nm) or Thorlabs (520 nm) pump beam was co-aligned 100 µm to the right of the probe beam as it passes through the sample in a counter propagating position to minimize crosstalk with the probe beam in the detector. Each laser was set to their max power: 140, 100, 120, 100, 40, or 120 mW for the OBIS 637, 640, 647, 660, 685 nm or Thorlabs 520 nm lasers, respectively. The beam was aligned by moving a right angle prism with a Newport 850A linear actuator. Lenses with long focal lengths are used to focus the beams at the edge of the quartz cuvette containing the CdSe/ZnS colloid. Angular deflections of the HeNe probe beam, which are caused by thermally-induced refractive index gradients in the colloid, are measured using a position sensitive detector and recorded using an oscilloscope or Stanford Research SR530 dual phase lock-in amplifier. An optical chopper was set to 18.3 Hz to modulate the pump beam.

2. Results and discussion

2.1. Photothermal deflection results

Photothermal results for the anti-Stokes wavelengths, i.e., 637, 640, and 647 nm, are shown in Fig. 2(a). Here, the black square wave signal shows when the laser is "on" and "off". It should be noted that the 660 nm laser produced a very weak signal, while the 685 nm laser produced no detectable signal. As such, neither of these results is shown. Fig. 2(b) shows the photothermal deflection spectroscopy results for the 520 nm Stokes wavelength. If we compare the results in Fig. 2, one can see an unmistakable 180° phase difference between the anti-Stokes and Stokes waveforms. This indicates that the positive temperature gradient (heating) produced