Femtosecond pulsed lasers have become an invaluable tool for examining ultrafast nonequilibrium dynamics. With pulsewidths of a few hundred femtoseconds (fs) to less than 10 fs, these lasers can clearly provide unprecedented temporal resolution. By amplifying ultrashort laser pulses to sufficient levels of energy per pulse, it is possible to exploit the nonlinear optical properties of certain materials to generate extremely broadband pulses. These pulses retain the time structure of the incident pulse, but contain a spectral bandwidth extending from the infrared to as far as the ultraviolet. By generating white-light pulses, it becomes possible to probe ultrafast nonlinear processes over a large range of energies. In this paper, the process of generating white-light ultrashort pulses will be presented, along with a discussion of different probing techniques and procedures necessary for modeling the transient optical data. Finally, results from pump–probe measurements using a white-light probe on indium phosphide (InP) films will be presented as a demonstration of this technique.

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Keywords: White-light; Femtosecond; Ultrashort lasers; Pump-Probe; Nonequilibrium

1. Introduction

Ultrashort pulse lasers, such as modelocked Ti:Sapphire oscillators, with pulsewidths on the order of a 100 fs (femtosecond) or less provide a fantastic tool for probing nonequilibrium dynamics with unprecedented temporal resolution. One of the best methods used in this pursuit is the pump–probe technique in which each laser pulse is split to produce an excitation pump pulse and a diagnostic probe pulse. Typically, the path of the pump pulse is fixed while the probe pulse path can be varied to measure the optical properties of the excited sample as a function of the relative delay between the pump and probe pulses. This type of experimental setup provides a very sensitive signal (changes in the probe reflectance as small as 10⁻⁶ are possible) and temporal resolution limited only by the pulsewidth [1]. It can be used for a wide array of applications in the fields of physics, engineering, chemistry, and biology on solid, liquid, or gaseous samples. In the context of the discussion presented here, the focus will be limited to application of the pump–probe technique to the examination of nonequilibrium dynamics in solid-state materials and films. For example, measurement of the transient optical response of semiconductor films can be used to determine the rates of several relaxation processes of photoexcited electrons [2–4]. In thin metal films, the technique can be used to measure the thermal diffusion properties, which have been shown to differ from those measured in the bulk material [5,6]. Also, measurement of the thermal boundary resistance across the film–substrate interface is possible using this technique [7].

In the most basic configuration described above, the pump and probe pulses are spectrally identical and the probe pulse interrogates the same states and transitions that are resonant with the pump pulse. Often though, it is of interest to examine states away from those resonant with the pump excitation to observe the evolution of processes initiated by the absorption of the pump pulse, such as electron–phonon (e–p) and electron–electron (e–e) scattering, recombination and trapping of excited electrons, as well as diffusion processes. To achieve this, it is necessary to modify and tailor the spectral content of the probe pulse to match the energy range of interest. This can be accomplished by exploiting the novel nonlinear optical phenomena that can be realized with the high electric field strengths found within ultrashort laser pulses. One possibility is...
to generate extremely broadband or white-light pulses by focusing high power ultrashort pulses through certain transparent materials [8–10]. These white-light pulses maintain the temporal characteristics of the input pulses and are quite easy to generate, requiring only a few optical components. While optical parametric amplifiers (OPA) are capable of producing higher power pulses with well defined narrow band spectral characteristics, they are extremely expensive and alignment presents a significant challenge for the user. In many cases, it is perfectly acceptable to use a broadband white-light probe, and when this is possible, the technique presented here provides a very easy pump–probe setup that enables probing from the visible to the infrared.

2. White-light pulse generation

By amplifying Ti:Sapphire pulses to sufficiently high energy, generally hundreds of nanojoules per pulse or greater, two nonlinear processes can be initiated in numerous materials, self-phase modulation (SPM) and Kerr lensing. Both processes rely on the intensity dependent nonlinear index of refraction, which is pronounced in crystals exhibiting inversion symmetry and in systems exhibiting microscopic disorder such as liquids and gases [11]. In this case, the full index of refraction is defined as:

\[ n = n_0 + n_{nl} I \]  

(1)

where \( n_0 \) is the normal linear index of refraction, \( n_{nl} \) the nonlinear index of refraction, and \( I \) is the intensity of the laser pulse [12]. When a laser pulse is focused through such a medium, the intensity dependent index of refraction causes increased focusing of the beam, or Kerr lensing [8,11]. To understand how the nonlinear term in the index of refraction gives rise to a modulation of the phase of the electric field, it is useful to examine the electric field vector of a laser pulse with a Gaussian intensity profile, \( I(t) \), propagating in the z direction:

\[ E = E_0 e^{i(\omega_0 t + \varphi)} = E_0 e^{i(\omega_0 t + \varphi)} e^{i(n_{nl} I(t)/c)z/v} \]  

(2)

where \( \omega \) is the angular frequency of the electric field and \( c \) is the speed of light. The time dependent intensity can thus be seen to cause a phase modulation proportional to the laser pulse intensity and the magnitude of \( n_{nl} \). This is the source of the SPM, which generates the broadband white-light spectrum extending from shorter wavelengths (anti-Stokes shifted) to longer wavelengths (Stokes shifted), though the intensity distribution is slightly asymmetric in favor of the short wavelengths [13].

As indicated, SPM can occur in any transparent solid-state media with inversion symmetry or in liquids and gases. Sapphire has been found to be an excellent material for generating stable white-light pulses. Although liquids such as water or ethanol do not suffer from damage, which can be a problem over time with sapphire, the white-light generated in liquids has excessively high spatial instabilities. This is very problematic since it causes fluctuations in the location of the probe spot on the sample surface, which will be manifested as additional noise on the signal. For this reason, solid-state media such as sapphire, LiF, CaF<sub>2</sub>, and other inversion symmetric crystals are recommended for generating white-light pulses for pump–probe experiments.

3. Application to the pump–probe technique

Having discussed the production of ultrashort broadband white-light pulses, it is important to examine the implementation into a pump–probe setup. A schematic of the experimental setup in the Microscale Heat Transfer Laboratory at the University of Virginia, which can be used to examine both transmissive and reflective samples is shown in Fig. 1. As in most pump–probe experiments, the laser output is split into a stronger pump beam and a weaker probe beam. The pump beam is modulated, in this case with an acousto-optic modulator, and focused onto the sample surface, creating a modulated excitation region on the sample. The probe beam passes through a half wave plate to rotate the polarization 90° and the beam is then folded onto a dovetail prism mounted on a linear translation stage with a positioning accuracy of 1 µm, or 6.67 fs of delay, well below the temporal resolution of the experiment. The delay stage provides a total of 1500 ps of delay for the probe path. Following the delay stage is the white-light generator, where the beam is focused by a 50 mm focal length lens through a high purity single crystal sapphire window. The white-light beam diverging from the sapphire window is collimated with an achromatic doublet, which enables proper collimation over a large range of wavelengths. Also, since there is a significant amount of the 800 nm fundamental wavelength that is not converted into a broadband spectrum, it is necessary to reject this portion of the probe beam with an 800 nm high reflector (HR).

The white-light probe beam is focused onto the sample surface at the center of the pump focus with a pump:probe spot size ratio of 5:1. Depending on the thickness and transparency of the sample, the probe beam is either reflected from the sample surface or transmitted through. The probe beam is then collimated and passes through a polarizer aligned to pass the probe polarization to improve the signal to noise ratio. There are several methods of signal detection for the probe, which have been broadly depicted as a spectroscopic detection system. In general though, all of these schemes utilize a diffraction grating to spread out the spectrum of the probe beam. This can be achieved using a fairly expensive spectrometer, or more simply with a basic monochromator scheme and a detector, either single element, or array. With a monochromator, the width of the entrance and exit slits defines the bandwidth passed to a single element detector for measurement. Using an amplified detector sensitive in the spectral region of interest, this setup gives the best signal, but if an array detector is employed, the exit slit is removed, and it is then possible to collect data over a range of wavelengths, simultaneously. A calibration of the detector array is straightforward knowing the pixel spacing and array size along with the span of wavelengths incident on the detector array. Array detectors do not always provide the spectral sensitivity or gain required for some experiments, but when it is possible to use this
system, it provides an extremely fast data collection system. In all cases, the data is presented as $\Delta R/R$ (transient change in reflectance) or $\Delta T/T$ (transient change in transmittance), by dividing the modulated AC signal by the DC signal on the detector. Also, when using a high repetition rate amplifier system, such as the Coherent RegA system shown in Fig. 1, it is also possible to achieve extremely high data acquisition rates using a lock-in detection scheme.

Having presented the setup for white-light probing, it is now important to address several considerations that must be made when modeling or interpreting the data. Depending on the spectral range of interest and the sample makeup, the nominal index of refraction over the range of probe wavelengths may vary sufficiently to affect the interpretation of the signal. To begin with, since the field strength of the probe interacting with the sample is not high enough to cause any nonlinear effects, we need only consider the normal index of refraction,

$$n_0 = n_1 + in_2,$$

where $n_1$ is the real part that causes refraction, and $n_2$ the imaginary part that gives rise to absorption. In optically thin transmissive samples, changes to $n_2$ are the primary factor affecting the $\Delta T/T$ signal, but often it is more useful to consider the surface response of nontransmissive bulk and thin film samples by interpreting the $\Delta R/R$ signal. In this case, it is necessary to consider both $n_1$ and $n_2$ over the spectral range of interest. In many metals, the overlapping band structure gives rise to a first interband transition which occurs at just a few hundred meV. The existence of interband transitions and the large number of free carriers in these metal films results in $n_1$ and $n_2$ being generally smooth slowly varying functions through the near IR and visible. In this case, the response of the film can be expected to behave uniformly across the range of probe energies. For some metals such as gold, there are large kinks in both $n_1$ and $n_2$ within this spectral range due to the rather high energy of the first interband transition. When probing such metal films with a spectral range spanning this transition, different reflectance models must be applied when analyzing the data above and below this energy [14]. Indeed it has been shown that when probing below the 2.45 eV interband transition energy for gold, an intraband reflectance model must be used to properly address the electron scattering processes when computing the $\Delta R/R$ signal [14].

In semiconductor samples, this effect is far more pronounced for several reasons. Interband transitions dominate photon absorption in semiconductor materials for photon energies above the band gap ($E_g$), and are almost negligible for energies below [15,16]. The effect on the reflectance response above $E_g$ is primarily due to the blocking of interband transitions as states are filled by the pump excitation and subsequently emptied as the electrons thermalize, relax, recombine, and diffuse [3]. While free carrier absorption (intraband absorption) can be significantly increased by the large carrier density photoexcited by a pump pulse with energy greater than $E_g$, it is still much smaller than direct and indirect interband absorption above $E_g$. On the other hand, when probing below $E_g$, free carrier absorption, which is mediated by e–p scattering, is the only process possible and thus can be isolated for examination. Herein lies one of the key benefits of white-light probing. By pumping a semiconductor film above $E_g$, a large density of free carriers is generated, and can be probed either above or below $E_g$, essentially isolating the processes and transitions of interest.

In modeling the $\Delta R/R$ data, care must be taken to properly compute the change in the probe reflectance properly. While the reflectance indeed occurs at the sample surface, it is affected by
the underlying electronic and crystal structure. Immediately following the pump excitation, a gradient of photoexcited carriers is generated normal to the sample surface (z direction) with a profile proportional to \( e^{-ax} \), where \( a \) is the absorption coefficient given by \( 4\pi n_d/\lambda \). In the case where \( E_{pump} > E_g \) and \( E_{probe} < E_g \), \( \alpha_{probe} \) may be much less than \( \alpha_{pump} \), and the gradient may need to be considered when developing a reflectance model [18]. If the magnitude of the gradient is small, or \( \alpha_{probe} \sim \alpha_{pump} \), then the gradient can be ignored and the pump excitation can be assumed to be uniform normal to the sample [19].

Far more important is the difficulty encountered when examining thin films on a substrate where the absorption depth of the probe, \( d_{film} \), is near to or even less than the film thickness, \( d_{film} = \frac{1}{a} \). In this case, reflected probe radiation from the film–substrate interface interferes with the film surface reflection and can significantly alter the signal [20]. When this is the case, a thin film reflectance model must be employed that carefully addresses the interference of the multiple reflections. When thin films become significant, small changes in the angle of incidence of the probe, film thickness, or the substrate index of refraction can have a dramatic effect on the \( \Delta R/R \) signal. Determining the proper thin film reflectance model presents perhaps the most difficult challenge when modeling the reflectance data.

4. An example application and results

The setup shown in Fig. 1 has been tested in the Microscale Heat Transfer Laboratory to model the \( \Delta R/R \) response of indium phosphide (InP) films. A monochromator and single element detector configuration was chosen for these experiments. The reflected probe beam was focused with a 50 mm lens into an Oriel 77250 monochromator, providing a near ideal match to the \( f \)-number of the monochromator in order to achieve the highest diffraction efficiency and maximum throughput. With 120 \( \mu \)m entrance and exit slits and a diffraction grating with a 600 line/mm pitch and a 1600 nm blaze angle, a 1 nm bandwidth signal was incident on the detector. The detector used was a Thorlabs PDA55 amplified Si PIN diode detector with the gain set as high as possible while maintaining a fast enough response that the detected signal was fully recovered before the arrival of the next pulse. The incident pump and probe pulses were measured as well during the data collection and used to remove noise from the signal by applying a phase correction scheme presented previously by Stevens et al. [21].

To demonstrate this technique and the modeling of the experimental data, measurements are presented for a 2142 nm thick single crystal InP film grown by low-pressure metal–organic chemical vapor deposition (LPMOCVD) on a sulphur doped InP substrates at 630 °C [22]. With \( E_g \sim 1.32 \text{eV} \), the pump energy of 1.55 eV is sufficient to photoexcite electron–hole pairs with excess energy that must be lost through relaxation of the electron system, primarily through e–p scattering before recombining can occur [23,24]. It is thus possible to isolate the free carrier response by probing at energies below the band gap. This is achieved by using achromatic doublets designed for the near IR range after the white-light generator. The phase corrected experimental data is shown in the contour plot in Fig. 2 where the darker colors indicate a stronger \( \Delta R/R \) signal. It can be seen that there is a large peak in the signal roughly centered at 945 nm, or 1.313 eV, in close agreement with the reported band gap for bulk InP at 1.32 eV.

In conjunction with other studies in the Microscale Heat Transfer Laboratory, a complete model describing the nonequilibrium dynamics of the thermalization, relaxation, recombination, and diffusion of the photoexcited carriers in direct gap semiconductors has been developed [19]. The approach taken in this model is to iteratively compute the number of photoexcited carriers, their total energy, and the spatial distribution normal to the film surface. Photoexcited carriers are generated by the source term that describes the absorption of a pump pulse and creates the nonequilibrium condition, which drives the dynamical processes. With each iteration of the model, the evolution of the excited carrier distribution due to these dynamical processes is calculated. The size of the time step used for each iteration is determined by the rate of the dominant processes. Initially, time steps of 5–10 fs are necessary to properly capture the source term as well as the thermalization processes, but as the model progresses, time steps of tens of hundreds of femtoseconds are used to accelerate the modeling code.

Computing the energy and spatial distribution of the excited carriers for each iteration is only part of the modeling process. At each time step, the change in the electric susceptibility (\( \chi \)) at the surface of the film is calculated using an optical model that has been developed for semiconductor materials [19]. This optical model addresses both the interband and intraband processes for the material and the complex index of refraction \( n_1 \) and \( n_2 \) is then computed from \( \chi \) at each time step. It was important to use the white-light probe setup to fully characterize the dynamical and optical models by probing both above and below the band gap, thus measuring the inter- and intraband processes individually. Before computing \( \Delta R/R \) from the modeled values for \( n_1 \) and \( n_2 \), it must be noted that the film thickness is comparable to the absorption depth, and thus a thin film reflectance model had to be used. The reflectance from thin film
structures has been addressed by Abele’s for several categories of substrates [20]. Following this approach, the modeled values for $\Delta R/R$ have been computed and show reasonable agreement with the experimental data. This is best demonstrated by looking at the normalized signal for both experimental and modeled data for some time delay after the signal peak. This is shown in Fig. 3 above for a time delay of 500 ps. One source of error in the modeled data is that the model assumes a perfect discontinuity at the interface whereas the real interface is certainly not as ideal, which may spoil or alter the interference effect predicted by the model. It is not clear how reflections from the real film–substrate interface compare with those in the reflectance model. This is an issue that would need to be addressed by a systematic study of the measured reflectance of well characterized real film–substrate interfaces.

5. Conclusions

The white-light pump–probe technique described here is a powerful tool for observing and measuring ultrafast nonequilibrium dynamics due to the photoexcitation of electrons at the surface of many different types of semiconductor and metal samples. It has been shown to be a relatively inexpensive setup that is straightforward to align. It also is capable of providing extremely fast data acquisition rates when implemented with a high repetition rate regenerative amplifier and even faster data collection if configured with an array detector to measure a large range of spectral data simultaneously. The experimental results presented here agree well with the expected optical response of InP near the band gap energy, and have been successfully modeled using calculations to predict the nonequilibrium dynamics of the electron system, the transient optical response, and the thin film reflectance accounting for interference effects due to reflections from the film–substrate interface.

References

[22] Samples prepared by J. L. Hostetler (all samples used for this study were grown and characterized at Trumpf Photonics, Inc., Cranbury, NJ 08512).