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Original Article

Application of Pump-Probe Technique for Tracking of Charge Carrier Relaxation In Nanostructured Semiconductors

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Abstract: The pump-probe technique is a powerful tool for probing and characterizing the electronic and structural properties of short-lived excited states of materials. Upon the absorption of photons of the pump, excited states of the materials are established. Relaxation of these states reflects many physical aspects of the materials which can be tracked by a consequent beam – the probe. In this paper, we present a conventional pump-probe technique at the University of Amsterdam and its application for tracking relaxation of charge carriers in thin films containing Si and Ge nanocrystals embedded in SiO_2 matrix. The pump beam is obtained from a 150-fs laser pulse with the photon wavelength at 340 nm. The probe beam is constituted from a white-light beam in the wavelength range from approximately 900 - 1300 nm (0.9 - 1.4 eV). The photon-generated charge carriers feature with multi-exponent decay dynamics, involving to different physical characteristics. The fast decay components of about few ps time scale arise from defect-related trapping or Auger processes, while the slow decay components of about few hundred ps come from relaxation of the exciton left in the semiconductor nanocrystals. The deep-insight characterization of the materials involving to individual relaxation processes are presented and discussed.

Keywords: Pump-probe technique, Si-Ge nanocrystals, photon-generated carriers, relaxations.

1. Introduction

Photoexcitation of a semiconductor leads to the generation of electrons in the conduction band (CB) and holes in the valence band (VB). Initially, these charge carriers are not in thermodynamic equilibrium

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because the absorbed light is required to match the energy of excited carriers [1]. The cooling of the electrons and holes occurs through carrier-phonon scattering, defects-assisted trapping, and/or Auger recombination processes [2–4], bringing the these charge carriers to thermodynamic equilibrium. Left electrons and holes bind together forming excitons, subsequently recombine to emit light. The carrier cooling processes may interpret many physical aspects and the electronic band structure of the material.

In an indirect bandgap semiconductor, e.g. Si and Ge, the difference in the momentum of electron and hole leads to a negligibly radiative recombination. The fast cooling processes of charge carriers occurs mostly non-radiatively via the phonon-carrier interaction, defect trapping or Auger process. At nanoscales, confinement effect of the charge carriers could help to improve the light emission [5–7], however, many unexpected factors arise causing new physical phenomena [3,4]. The pump-probe technique enables us to measure ultrafast charge carrier cooling processes inside the semiconductors thanks to very fast laser pulses. An intense laser pulse of the pump beam in the time scale of about fs is sent on the object to excite it. The second and weaker pulse of similar or different wavelengths, the probe beam, comes right after. The change in the absorption intensity of the probe is detected and resolved to help estimating the influence of the pump on the sample. The temporal delay between the pump and probe pulses can reconstruct the evolution of carriers cooling processes, reflecting the relative number of photo-generated carriers versus time.

In this paper, a conventional pump-probe setup at the University of Amsterdam used in this study is presented. By using this setup, experimental method results on the tracking of the photon-generated carriers in sputtered Si and Ge nanocrystals are reported. Carrier cooling processes, and physical phenomena occurred in the materials are demonstrated and discussed.

2. Experiment

2.1. Methodology

In principle, in the conventional pump-probe experiment, also known as transient induced absorption, the intensity of the probe is measured by the induction of the pump in the sample. In this part, the pump-probe setup at the University of Amsterdam, the Netherlands, used for all the experiments in this study, is presented. The schematic diagram of this pump-probe setup is depicted in figure 1.

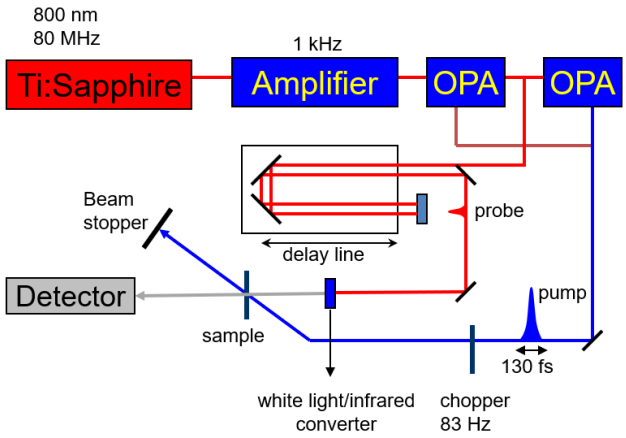

Figure 1. Schematic diagram of the pump-probe setup at the University of Amsterdam used for all the TIA experiments in this study.

A chirped-pulse amplified titanium-sapphire laser (Ti:Sapphire), 800 nm and 80 MHz, pumps optical parametric amplifiers (OPA) to tune the primary pulse to excitation photon energy of 340 nm. The secondary pulse is guided through a white light near-infrared converter to create a broadband probe beam in the range from 900–1600 nm (1.35–0.9 eV) to probe the photon-generated charge carriers in the sample. Temporal delay between pump and probe pulses is controlled via a white light retroreflector. The transmission of the probe is recorded by a CCD camera following the equation:

$$I_{probe} = \frac{I_{pump+probe} - I_{lin.abs.probe}}{I_{lin.abs.probe}} \times 100\%, \quad (1)$$

in which, the signal of the probe (I_{probe}) under influence of the pump (Ipump+probe) is detected, after which the linear absorption ($I_{lin.abs.probe}$), so the probe signal without the pump is subtracted and then normalized for the linear absorption. In this way we only detect the change of the probe signal under influence of the pump. Dimensions of the pump spot size were chosen to be considerably larger than those of the secondary pulse to assure complete overlap for all delay settings. All the pump-probe experiments in this study were performed at room temperature.

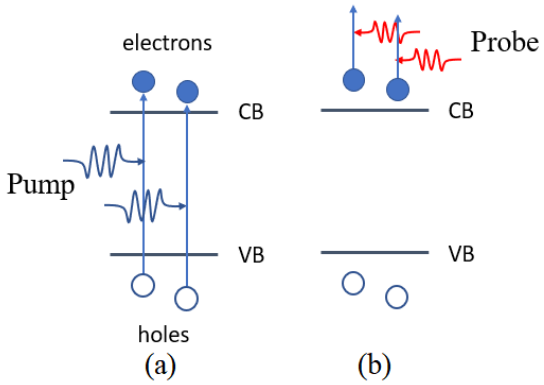

Figure 1. The dynamics of charges carriers in a semiconductor under a pump (a), consequently probed by a probe beam (b) after a temporal time between the two beams.

Figure 2 demonstrates interaction of the charge carriers in a semiconductor under the influence of the pump and probe beams. Upon the absorption of the pump beam, electrons move to CB and leave holes in VB (a). Instantly, the photo-generated charge carriers will relax to the thermodynamic equilibrium within ps time scale depending on materials. Consequently, the photo-generated charge carriers are absorbed photons of the probe beam and jump to higher energy states (b). In such the way, absorption intensity of the probe beam, the induced absorption, reflects the number of photo-generated charge carriers remained in the excited states or their relaxation process.

2.1. Samples

Samples used in this study were prepared by co-sputtering method on AJA ATC Orion system with three confocal cathodes of SiO_2, Si, and Ge. Sputtering proceeds under argon plasma at the pressure of 3 mTorr with a background pressure down to below 5×10^{-7} Torr. Ratios of between Si and Ge was set by sputtering power on individual guns to contribute to about 30 vol.% excess Si–Ge in SiO_2. Subsequently, the as-grown samples were annealed at 800 °C in continuous-flow N_2 gas for 30 min for crystallization. More details on the samples preparation and some characterizations can be also found elsewhere [8,9]. Two samples containing pure GeNCs and Si-Ge alloy NCs with the Si:Ge ratio of 3:2

entitled with GeT800 and Si_4Ge_6T800, respectively. The crystal sizes of all samples in the range from about 5-10 nm were estimated via X-ray diffraction patterns by using Debye-Sheerer equation and reported in the independent studies [8,10].

3. Results and Discussion

Figure 3 shows transient induced absorption of the photo-generated charge carriers in the sample Si4Ge6T800 recorded at the probe photon energy E_{probe} = 1 eV (1240 nm). We see that the photo-generated charge carrier relaxation process consists of multiple decay exponents. Red line is the multi-exponential fitting with the following equation:

$$I = \sum_i^3 A_i e^{-\frac{t}{\tau_i}}, \quad (2)$$

where, τ_i is the lifetime of photo-generated charge carriers in the sample corresponding to decay component *i* and A*i* is the amplitude of individual decay components. Each decay component arises from a different relaxation process involving to different physical aspects. We see that the TIA intensity drastically decreased in within few ps time scales with τ_1 = 0.5 ps time scale. The second and the third decay components have lifetimes of τ_2 = 10 ps and τ_3 = 500 ps, respectively. Amplitudes of the slow decay components are order of magnitude smaller than the intensity of the fast component.

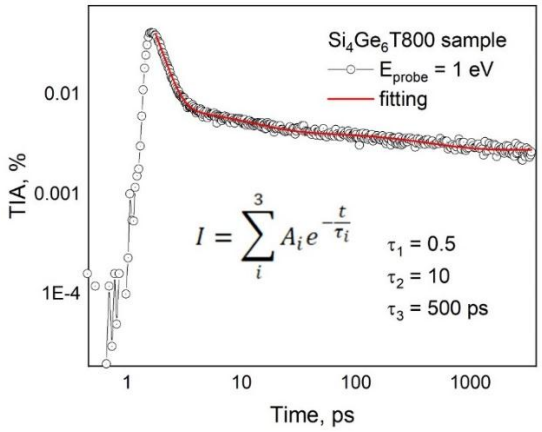

Figure 3. Decay dynamics of photo-generated charge carriers recorded with probe photon wavelengths at 1240 nm (~ 1eV) for the sample Si4Ge6T800

The high amplitude of the fast decay component implies that most of the photo-generated charge carriers dissapeared fast within few ps after the excitation by the pump beam. The slow decay component corresponds to recombination of the single exciton left in the NCs [11]. In the previous report [4], we have shown that the fast decay component was identified for the trapping of photo-generated charge carriers by defects in the boundary of the SiGe NCs and the surrouding SiO_2 matrix and/or Auger recombination of the excited charge carriers. A similar behavior is observed in the current work, however slow component is fitted with a lifetime of about 500 ps. This fitted lifetime is shorter than the slow component in the previous report [4] where a large error might occured.

Figure 4 present TIA spectra with different interval times measured for the sample Si_4Ge_6T800. The hump at the probe photon wavelength at around 1100 nm initially appeared, then moving towards the

short wavelength with the increasing interval time. The red dotted line is for the eye-guiding purpose. This behavior is not understood at present. We see that the TIA intensity decrease drastically in within 10 ps time scale for all the probe wavelengths in the studied range. In our recent study [4], carrier traps with ionization energy of about 1 eV, characterized by a long-range Coulombic potential, were identified explaining the increased TIA intensity with the increased probe photon energy.

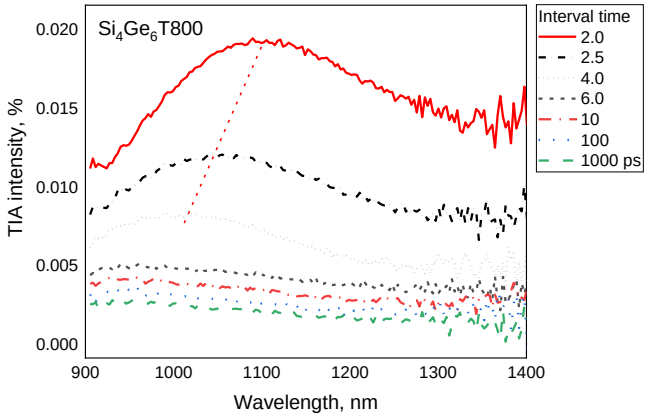

Figure 4. TIA spectra with different interval times measured for the sample Si_4Ge_6T800. The red dotted line is for the eye-guiding purpose.

Figure 5 present the TIA decay dynamics measured for the GeT800 sample with E_{probe} = 1.24 eV (~1000 nm). We observed that the photon-generated charged carrier decay dynamics features also with multiple-exponential components. The fast component has a time scale of about few ps time scale and overlapped with a deep valley ascribed for ground-state bleaching commonly seen in similar systems [3,12]. We exclude the stimulated emission in the prepared GeNCs since there were no significant PL signal was recorded at the E_{probe} = 1.24 eV.

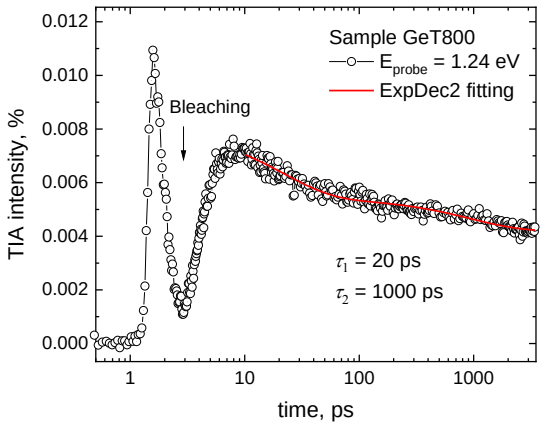

Figure 5. TIA decay dynamics measured for the GeT800 sample with E_{probe} = 1.24 eV. Red line is the multiple-decay fitting.

This bleaching effect disappeared after about 5 ps which is much shorter than that of similar materials [3,12]. However, defects and fast carrier trapping were concluded in the Si-Ge alloys NCs [4],

the bleaching effect was not observed for the sample Si_4Ge_6T800. Red line is multiple-exponent decay fitting for slow components with two lifetimes of about 20 ps and 1000 ps. We see that the slowest component of pure Ge sample is two time longer than the slowest component of the Si-Ge alloy sample. This behavior may be explained by crystallinity where the crystallization of the pure Ge sample is better than the crystallization of the alloys. This is reasonable thanks to the fact that the melting temperature of Ge is smaller than the melting temperature of Si [8]. Thus, large Ge NCs formed in the GeT800 sample causing a long lifetime of the left excitons.

4. Conclusion

In this study, a conventional pump-probe technique, and its applications in the tracking of charge carrier relaxation were reported. Thin films containing GeNCs and Si-Ge NCs embedded in SiO_2 matrix were used as the studied objectives. The photo-generated charge carriers upon the absorption of the pump beam showed multiple-exponent decay components, concerning to different physical properties. Most of the charge carriers generated in the pump beam vanished after a few tens of ps because of Auger recombination and carrier trapping process which were quite popular in similar nanostructured semiconductors. Bleaching effect of GeNCs was also observed and consistent with the results shown in Ref. [3,12]. Although, many physical characterizations of the materials were presented but not fully understood, the pump-probe technique helped us to track the ultra-fast phenomena in the nanostructured semiconductors.

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