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THE UNIVERSITY OF WARWICK

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Re: Doctoral Thesis of Vit Zajac, Faculty of Mathematics and Physics, Charles University

Dear Examination Committee,

Please find enclosed a detailed report on the Doctoral Thesis of Vit Zajac on the "Ultrafast response of electrons in nanostructured and disordered semiconductor systems studied by time-resolved terahertz spectroscopy". I can confirm that the thesis represents a substantial contribution to the field and is of a very high quality, more than sufficient to warrant the award of a doctorate to the candidate. There are a number of original contributions to the field made by the candidate, which are presented with clarity in this thesis.

The submitted thesis is concerned with the use of time-resolved terahertz spectroscopy to study the dynamical conductivity of semiconductor nanocrystals of silicon, and the bulk material titanium dioxide. The introduction and motivation for the doctoral work is excellently written. The author has a clear and lucid style that describes in perfect detail the relevant background information, both about the experimental techniques used and the models use to understand experimental data. The background chapter on the use of THz spectroscopy to study nanomaterials is a clear and up-to-date summary of most of this growing field of research.

A key aspect of this work is the development of a new effective medium theory (the VBD model), which lets models of the experimental data be constructed from information about sample morphology, and takes as input various different microscopic conductivity models. The V, B, and D parameters refer to, respectively, the contribution to the conductivity of percolated material (V), a scaling factor that changes the microscopic conductivity of the nanoparticle (B), and a term that can be thought of as linked to the spacing and degree of coupling between nanoparticles (D) analogous to the capacitance. This new modelling work is of very high quality and is an important advance for the field, and can be intuitively derived by analogy to circuit theory. The author contributed to the development of this model and has a clear exposition of how it works, and how it relates to other existing effective medium models (such as the Maxwell-Garnet approach). The author has also contributed a substantial effort in the theoretical derivation of a solution to the wave equation describing THz radiation propagating through percolated and non-percolated nanomaterials, as presented in chapter 5, which is important and used in later chapters to understand details of the spectral response.

Chapter 6 presents the first set of experimental results of the thesis, which is on silicon nanocrystals fabricated from nanoporous silicon. The silicon nanocrystals have a large silicon oxide shell, as shown by X-ray photoelectron spectroscopy (XPS). Here, the original contribution presented by the author is to perform a careful comparison of experimental data from time-resolve THz spectroscopy with detailed models using the VBD effective medium approach developed in Chapter 4. The sample morphology is examined, revealing a large distribution of particle sizes. The main conclusion is that THz spectroscopy appears to be more sensitive to the larger particles in the distribution, which may be small in number but which have larger volume. This is important as the experimental techniques typically applied to such nano-composites may miss these larger particles. The temperature-dependence of the THz response was explored. The Drude-like microscopic conductivity in conjunction with the B, D morphological parameters were used to simulate the THz mobility spectra.

This work is extended to silicon nanocrystal superlattices in Chapter 7. Instead of individual silicon nanoparticles with a large size distribution (Chapter 6), the adoption of a different growth methodology allowed narrower nanoparticles with a better controlled size distribution to be studied. The results are described well, and the experimental data are modelled accurately by the VBD effective medium model with a carrier mobility spectrum input from Monte Carlo simulations. Importantly, the parameters input are those of the bulk materials, or as independently measured by transmission electron microscopy. Some samples showed evidence for longer-range transport when clusters of silicon nanoparticles formed.

In Chapter 8 a study of bulk rutile TiO_2 at different temperatures and fluences is presented. This work includes an important extension and reinterpretation of some older work in the literature, using an improved modelling analysis that takes into account the diffusion of photoexcited carrier distributions into the bulk of the material, away from the surface. Both electron and hole contributions were included, and the density-dependent scattering time was parameterised. The results are discussed in the context of the strong polaronic mass enhancement in rutile TiO_2. The plasma diffusion model will most likely find widespread use in similar studies of other bulk compounds.

Chapter 9 presents a new extension of the group's Monte Carlo code to include the morphology of the nanosystem in fuller detail. A system of nanospheres on a cubic lattice was chosen in order to investigate mobility spectra on a model system with specific morphology, and to compare it with the previous probabilistic approach to carrier motion between nanoparticles.

In terms of the experimental approaches and conclusions drawn the thesis is quite robust and a solid case is put forward for the conclusions drawn. There are a few detailed points which I plan to query the candidate about in the Thesis Defense, such as the conclusions drawn about the composition of the silicon nanocrystal samples (Chapter 6) from the combination of AFM and XPS. I would also like to discuss in detail whether the approach taken of normalising the experimental transmission spectrum by the incident fluence, and presenting a mobility spectrum, is the most apt approach in all cases. In Chapters 4, 6 and 7 a non-linear dependence of the measured transient photoconductivity (of the effective medium) on pump fluence is stated to indicate uniquely that carriers are confined in non-percolated inclusions (or alternatively that ΔT_{norm} depending on fluence indicates this regime). This is not a unique conclusion, however – for instance a fluence dependent scattering rate would produce the same effect. Similarly, changes to the quantum yield with pump fluence, for instance as a result of band filling, bandgap renormalisation, or band non-parabolicity may contribute, particularly at the largest photoexcitation fluences used in these experiments. Another topic that may have been useful to include in the thesis is some background about the bandstructure of silicon, how rapidly electron relaxation occurs after photoexcitation at 400nm.

I conclude by re-iterating my recommendation that the Doctoral Committee award the degree of Doctor in Physics (PhD) to the candidate. This is an excellent piece of work: the thesis is a pleasure to read, and is highly informative about the state-of-the-art in this particular field. It also contains work that has already been published in internationally important journals.

Yours sincerely,

James Lloyd-Hughes

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