OD-XAS and EXAFS: Structure and Luminescence in Ge Quantum Dots

A Karatutlu\textsuperscript{1,*}, W R Little\textsuperscript{1}, A V Sapelkin\textsuperscript{1}, A Dent\textsuperscript{2}, F Mosselmans\textsuperscript{2}, G Cibin\textsuperscript{2} and R Taylor\textsuperscript{2}

\textsuperscript{1} Centre for Condensed Matter and Materials, School of Physics and Astronomy, Queen Mary, University of London, London, E1 4NS, United Kingdom

\textsuperscript{2} Diamond Light Source Ltd, Rutherford Appleton Laboratory, Didcot, OX11 0DE, Oxon, United Kingdom

*Ali Karatutlu, email: a.karatutlu@qmul.ac.uk*

Abstract:
The source of visible luminescence from Ge nanocrystalline materials has been attributed to various phenomena such as the quantum confinement effect, surface contributions, and so on. In order to understand the origin of this light emission we have performed extended x-ray absorption fine structure (EXAFS) and optically-detected x-ray absorption spectroscopy (OD-XAS) using x-ray excited optical luminescence (XEOL) measurements on a range of Ge quantum dots prepared by various routes including stain etching, sol-gel method, and laser ablation. Such XEOL and OD-XAS studies on Ge and Ge-O rich regions allowed us to determine specific local sites responsible for PL.

1. Introduction
Reducing the size down to a certain value, known as the Bohr exciton radius for a semiconductor (for example silicon [1], or germanium [2]) causes significant changes in the light emitting properties due to the well known quantum confinement effect. Shortly after these discoveries it became obvious that the photoluminescence in Ge nanocrystals is not only size dependent but also may be due to surface species such as oxides and hydrides, or defects [3]. It has been over two decades since the effect was first observed but the topic is still contentious as direct observation of the source of the photoluminescence (PL) is challenging despite intense research [4].

Extended x-ray absorption fine structure (EXAFS) by transmission mode is accepted as a conventional local structural measurement technique [5]. This technique enables one to determine chemical composition, interatomic distances, and number of neighbours around the absorbent atom [6]. Here we used a technique known as optically detected x-ray absorption spectroscopy (OD-XAS) using x-ray excited optical luminescence (XEOL) to probe the substructure responsible for the light emission. To this end simultaneous OD-XAS and EXAFS measurements were taken, including XEOL from Ge nanoparticles. The nanoparticles were prepared by various routes such as stain etching, liquid-phase...
pulsed laser ablation (LP-PLA), and sol-gel method. Characterisation of the Ge nanoparticles has also been performed using transmission electron microscopy, and Raman and PL spectroscopy techniques.

2. Experimental Procedure
Ge powder, supplied by Sigma-Aldrich, of over 99.999 % purity was used for both stain (chemical) etching and LP-PLA. Stain etching was performed with the solution of HF:H₃PO₄:H₂O₂ having the chemical volume ratio of 15 ml:15 ml:0.075 ml respectively which was found to be optimal in [7]. The procedure took place over 3 hours under indoorfluorescent illumination. For LP-PLA a Nd:Yag (Surelite I-10) was used. Using a combination of dichroic mirrors the beam was focused to an area of 4x1 mm² inside a quartz cuvette filled with n-hexane. The output of the laser was kept at 108 mJ. The pulse frequency and the pulse duration were 1 Hz and 13 ns respectively. The cuvette contained 17 mg of Ge powder and n-hexane to a depth of a 1.5 mm. Laser Ablation was performed for 7 hours. The hexane was allowed to fully evaporate before suspending the residue in ethanol and centrifuging to separate the germanium nanoparticles from the remaining Ge powder. The method for sol-gel synthesis [8] of Ge nanoparticles embedded in silica (SiO₂) is three successive processes including the sol-gel method, and then 48 hours of heating treatment in air at 600 °C, followed by a heating treatment in H₂(5%)/Ar(95%) medium at 700 °C.

Raman spectroscopy, PL spectroscopy (Renishaw 1000) and TEM measurements (JEOL JEM 2010 Microscope) of the resultant product have been analyzed in order to find the size of Ge nanoparticles prepared by the each route. OD-XAS and EXAFS including simultaneous XEOL measurements of the same area of each sample have been carried at beamline B18 at Diamond Light Source UK. The equipment for OD-XAS includes a TRIAX180 spectrometer, a photomultiplier tube, Hamamatsu R3809U-50 MCP in addition to an X-ray detection system (details given in the appendix) in order to record the X-ray emitted luminescence. For OD-XAS and EXAFS, the Ge K-edge was recorded as a function of energy over the range of 11.05-12 KeV. XEOL measurements were collected from the same area as a function of wavelength centered at 700 nm for the each set of the samples. Demeter 0.9.8 [9] was used for EXAFS analysis.

3. Results and Discussions
We present the details of the size analyses and how to distinguish various subsets of Ge nanoparticles by OD-XAS and EXAFS measurements. Raman spectra of Ge nanoparticles formed by (a) stain etching, (b) sol-gel synthesis and (c) LP-PLA have been studied for the size analyses and shown in figure 1. The analyses have been performed under the assumption of the phonon confinement model [10].

![Figure 1](image1.png)

**Figure 1** Normalised Raman Shift of Ge nanocrystals from right to left (a) bulk Ge and by using (b) stain etching, (c) sol-gel method and (d) LP-PLA.

![Figure 2](image2.png)

**Figure 2** XEOL at 100 °K of the Ge nanoparticles prepared by (a) stain etching, (b) Sol-gel method, (c) of the bulk Ge.
The size of the Ge nanoparticles fabricated by stain etching, sol-gel synthesis and LP-PLA were found to be approximately 6 nm, 5 nm, and 6 nm respectively both from TEM and Raman measurements. Raman measurements in figure 1 showing that the Ge nanocrystals [11] synthesized by these routes are of a similar size. XEOL signals in figure 2 gives some indication of differences in the origins of sites responsible for light emission. Further, OD-XAS reveals the different subset of the structures which are optically active at around 700nm.

Here we identify the origin of the PL from the structural data by using OD-XAS. A clear difference was observed by comparing OD-XAS and EXAFS in R-space over the Ge K edge shown in figures 3(b), 4(b), and 5(b). In figure 3(b), OD-XAS probes native oxide sites in bulk Ge. Furthermore, in figure 4(b) the Ge nanoparticles formed by LP-PLA reveals that the optical contribution is primarily from the GeO$_2$ region. However, in figure 5(b), EXAFS and ODXAS of Ge nanocrystals embedded in SiO$_2$ are almost identical until 3 Å. There are limits to sensitivity in a multicomponent system with various emitting sites [12]. Figure 6 indicates that OD-XAS is sufficiently sensitive to contributions from Ge nanoparticles synthesized by stain etching, LP-PLA and sol-gel method. In the case of stain etching, the main contribution to the PL is due to Ge atoms with an inter-atomic spacing
of $2.44\pm0.01$ Å which only differs by $0.09$ Å from EXAFS of Ge K edge of bulk Ge, shown in figure 6(d).

4. Conclusion

OD-XAS is found to be a very promising technique for achieving the specificity of the sub-nanoparticle resolution when investigating Ge nanoparticles synthesized by various routes. We show that by using OD-XAS and EXAFS on the Ge K edge the subsets of the structure responsible for the emission process have been determined. The main difference between OD-XAS and EXAFS stems from the fact that OD-XAS probes only the sites of the sample that contribute to light emission, as in the case of sol-gel method and LP-PLA or structurally disordered sites of nano-crystalline germaniums in the case of stain etching. Despite having shown how the subsets of the structure contribute to the final decay process, the exact process for excitation and emission is not yet completely understood. Particular attention is drawn to the roles played by the surface, the interfacial region, and the core.

5. Acknowledgement

The following are greatly acknowledged by the authors: the financial support by the Queen Mary, University of London Research Fund and SEPnet and, V. T. Karavanski (for stain etching sample preparation).

6. Appendix

The details and supplementary results are given in this part of the paper.

7. References

[1] Canham L T 1990 Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers Applied Physics Letter 57 1046-1048
[2] Maeda Y, Tsukamoto N, Yazawa Y, Kanemitsu Y and Masumoto Y 1991 Visible photoluminescence of Ge microcrystals embedded in SiO$_2$ glassy matrices Applied Physics Letters 59 3168
[3] Delerue C 1998 Optical band gap of Si nanoclusters Journal of Luminescence 80 65–73
[4] Daldosso N, Luppi M, Ossicini S, Degoli E, Magri R, Dalba G, Fornasini P, Grisenti R, Rocca F, Pavesi L, Boninelli S, Priolo F, Spinella C and Iacona F 2003 Role of the interface region optoelectronic properties of silicon nanocrystals embedded in SiO$_2$ Physical Review B 68 1–8
[5] Dowsett M G, Adriensa A, Jones G K C, Poohton N, Fiddy S and Nikitenko S 2003 Optically detected X-ray absorption spectroscopy as a means of monitoring corrosion layers on copper Analytical Chemistry 80 8717-24
[6] Erenburg S B, Trubina S V, Bausk N V, Dvurechenskii a V, Nikiforova I, Mansurov V G, Zhuravlev K S and Nikitenko S G 2009 Microstructure of quantum dots ensembles by EXAFS spectroscopy Journal of Physics: Conference Series 190 012131
[7] Karavanskii V A, Lomov A A, Sutyrin A G, Bushuev V A, Loikho N N, Melnik N N, Zavaritskaya T N and Bayliss S 2003 Raman and X-ray studies of nanocrystals in porous stain-etched germanium Thin Solid Films 437 290–6
[8] Henderson E J, Seino M, Puzzo D P and Ozin G A 2010 Colloidally Stable Germanium Nanocrystals for Photonic Applications ACS Nano 4 7683–91
[9] Ravel B, Newville M 2005 ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT Journal of Synchrotron Radiation 12 375–41
[10] Campbell H I and Fauchet P M 1986 The effects of microcrystal size and shape on the one phonon Raman spectra of crystalline semiconductors Solid State Communications 58 739–41
[11] Sapelkin A V, Karavanskii V A, Kartopu G, Es-Souni M and Luklinska Z 2007 Raman study of nano-crystalline Ge under high pressure Physica Status Solidi (B) 244 1376–80
[12] Emura S, Moriga T, Takizawa J, Nomura M, Bauchspiess K R; Murata T; Harada K; Maeda H 1993 Optical-luminescence yield spectra produced by x-ray excitation Physical Review B 47 6918–30

Appendix

The experimental details in addition to the complementary results are given in this part. Figure 7 shows PL signal from Ge nanoparticles produced by (a) stain etching, (b) LP-PLA, (c) sol gel synthesis.

![Figure 7](image)

**Figure 7** PL spectra of Ge nanoparticles formed by (a) stain etching (b) LP-PLA, (c) sol gel synthesis. Photoluminescence (PL) spectrum has been recorded from the each of the samples with excitation by HeCd laser at 473 nm.

TEM micrograph in figure 8 shows Ge nanoparticles formed by (a) stain etching, (b) LP-PLA and (c) sol-Gel Method. Size analyses in table 1 reveals that the size of the Ge nanoparticles prepared by stain etching and the sol-gel method are in agreement but those formed by LP-PLA are not, due to the agglomeration issue which results in particle sizes well out of the quantum confinement region (about 24 nm for Ge nanoparticles given in [2]).

![Figure 8](image)

**Figure 8** TEM micrograph of Ge nanoparticles from top to down prepared by (a) stain etching (b) LP-PLA and (c) Sol-Gel Method.
Table 1 Size analyses of the Ge nanoparticles by Transmission electron microscopy, Raman spectroscopy and PL spectroscopy.

| Method       | Transmission Electron Microscopy (nm) | Raman Spectroscopy |
|--------------|--------------------------------------|--------------------|
| (a) Stain Etching | 10 ± 4                               | 6.9 10             |
| (b) LP-PLA    | 41 ± 22                               | 6.2 12             |
| (c) Sol-Gel Method | 10 ± 6                               | 5.3 14             |

The equipment for OD-XAS includes also a photomultiplier tube, Hamamatsu R3809U-50 MCP in order to record the X-ray emitted luminescence using an optical fibre in addition to the detection system consisting of a Triax 190 spectrometer equipped with Synapse CCD and a Newport VIS Femtowatt photoreceiver. All measurements have been performed at a temperature of 100 K using a cryojet system.

For the fits of OD-XAS and EXAFS spectra of bulk Ge, the k-weight value such as 1, 2 and 3 is shown in figure 9. The best fit was obtained at k-weight 2 and the rest of the fittings were performed at k-weight 2 for the fits of each sample.

As an example of the fits performed for each sample with a k-value of 2, the fit for the Ge K edge of Ge nanoparticles formed by LP-PLA in R-space with the contributions from the each scattering path is given in figure 10.

![Figure 9](link-to-figure-9)

**Figure 9** OD-XAS of Ge K edge of bulk Ge in R-space at k-values 1, 2 and 3.

![Figure 10](link-to-figure-10)

**Figure 10** OD-XAS of Ge K edge of Ge nanocrystals formed by LP-PLA and the fit in R-space including the first three scattering paths.