3.1 Bericht Teilprojekt 6

3.1.1 Titel / Title

Photophysik und Photochemie an Grenzflächen von Silizium Nanoteilchen

Photophysics and photochemistry at interfaces of silicon nanoparticles

3.1.2 Berichtszeitraum / reported period

01.07.2003 - 31.12.2006

3.1.3 Projektleiter / principle investigator

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3.2 Zusammenfassung / Abstract

3.2.1 Wortlaut des Antrags / abstract of the proposal

Während der ersten Antragsperiode wurde demonstriert, dass eine Untersuchung auch einzelner Silizium Nanokristalle möglich ist. Bei optischer Anregung zeigen größenselektierte Partikel-Ensembles zeitabhängige spektrale Verschiebungen und Intensitätsveränderungen. Einzelne Nanokristalle zeigen Blinken in der Emissionsintensität. Diese Effekte werden auf den Einfluss der Nanokristallhülle bzw. auf die direkte Umgebung der Nanokristalle zurückgeführt. Die Mikrostruktur und chemische Zusammensetzung dieses Grenzflächenbereiches erzeugt Pfade auf denen photochemische Reaktionen, wie z.B. Ladungstransfer stattfinden können. Innerhalb dieses Projektes sollen die Experimente aus der ersten Antragsperiode auf eine systematische Untersuchung dieser Grenzflächeneffekte auch in Abhängigkeit einer durch AFM –Methoden bestimmten Größe erweitert werden. Dabei sollen die Grenzflächeneigenschaften mit Blick auf einfache astrophysikalisch Modellsysteme (Einbettung in molekulares Eis, PAH dotiertes Eis) gezielt variiert werden, um so Informationen über photophysikalisch-photochemische Prozesse an der Partikelgrenzfläche zu erhalten. Der enge Bezug zu astrophysikalischen Bedingungen schließt die Variation der Temperatur ein, die für viele Prozesse ein entscheidender Parameter ist.

During the last period the feasibility to investigate the spectroscopic properties of (single) silicon nanoparticles was demonstrated. Upon optical excitation size selected particle ensembles show spectral shifts and intensity changes. Single nanoparticles exhibit blinking behavior. These effects are thought to be closely related to properties at the interface of the particle with the environment. The microstructure and chemical composition of this interface create funnels via which photochemical reactions such as charge transfer may proceed. In this project we will extend the experiments of the first application period towards a systematic variation of the interface properties of the particles as a function of size determined via AFM methods with a close relation to simple astrophysical model environments. Such environments are mainly pure molecular ice and doped (polycyclic aromatic hydrocarbons) ice environments. Since temperature plays a key role for many astrophysical processes and can largely change between different interstellar regions, all experiments will be related to temperature variation.

3.2.2 Zusammenfassung des Berichts / abstract of the report

Since in the first period of the research work experiments have revealed that the photoluminescence (PL) dynamics were subject to a variety of photoinduced processes we concentrated on the investigation of the nature these processes. They depend strongly on the presence of the SiO_2 interface since in the absence of such an interface no PL is observed at all. We therefore investigated in the second period (i) porous silicon nanocrystals (prepared via electro-chemical etching followed by ultrasonic treatment) and (ii) silicon nanocrystals prepared in the gas phase via laser pyrolysis (Prof. Huisken, Jena).

Spectroscopic and dynamic information is more subtle in case of single particle detection. For this reason we concentrated during the second research period mainly on single particle investigations. Although it finally

turned out that single particle detection was only feasible for a limited range of PL energies (corresponding to crystal diameters between 2 nm and 3 nm), comparison of the overall dynamics (blinking and bleaching) shows that at least photoinduced dynamics are comparable over the total PL range of silicon nanoparticles, independently whether they have been determined from ensemble or single particle experiments.

However, spectroscopy on single silicon particles in the energy range from 1.9 eV to 2.45 eV revealed that as compared to ensemble experiments reported in the literature, the PL of small silicon particles is strongly influenced by electron-phon coupling to vibrations in the oxide shell. Additionally, the exciton becomes probably localized at energies above 1.9 eV. We can provide strong evidence, that electron and hole are independently localized at different crystalline sizes, thus settling an unsolved question frequently posed in literature.

3.3 Ausgangsfragen, neuster Stand der Forschung / Initial goals, current status of the field

The goal of the proposed project within the first period was the study of photophysical properties of silicon nanocrystals and relating these findings to the interstellar extended red emission (ERE) (Witt 1998, Smith 2002, Ledoux 2001). At that time the radiative pathways of the indirect silicon band gap emission were not understood. Especially the interrelation of silicon core and (SiO_2) capping shell were completely open.

For this reason the second period has been focused on the investigation of phenomena related to interface properties.

During the last three years the investigation of interface phenomena in nanocrystals has been intensively investigated for II/VI colloidal nanocrystals. Recent experiments and models (Issac 2005, Tang 2005) have provided strong evidence that photoejected electrons are trapped in the dielectric environment even outside the capping layers.

Additionally to the literature already cited in the previous report, new single particle experiments on silicon nanoparticles have been reported (Sychugow 2005). Independent of the existing possibility of the relevance of silicon photoluminescence for the ERE emission (Witt 2005) the clarification of photoinduced interface dynamics is still an open question not only with respect to astrophysics.

Concerning optical properties of silicon nanocrystals several papers related to exciton localisation (Garrido 2004, Heitmann 2004) and electron phonon coupling (Sa`ar 2005) have been published and have been considered to be a general base for our own detailed single particle investigations.

3.4 Angewandte Methoden / Experimental methods

One of the goals of the project was to apply single particle microscopy methods to study the photophysics of silicon nanocrystals. The reasons to apply these methods lie mainly in the strong inhomogeneous broadening of nanoparticle ensemble spectra due to the strong size dependence of single particle transition energies. Furthermore single particle emission shows an intermittency due to the existence of so called dark states, where the particle cannot emit. The use of single particle optical microscopy allows direct access to these dark periods and will therefore provide detailed information about the physical processes connected with the dark periods, which are indicative for photoinduced physico-chemical processes. Such processes are also expected in interstellar matter.

3.5 Ergebnisse und ihre Bedeutung / Results and their importance

In the previous report we could show that silicon nanocrystals either prepared from gas phase (in cooperation with Prof. Huisken, Jena (TP10)) or porous silicon particles exhibit photoluminescence (PL) properties which could be related to the ERE emission. Additionally, we reported PL dynamics which are subject to (reversible) photobleaching of the ensemble emission and PL intermittency (blinking) of porous nanoparticles. At that time we were not able to perform experiments on (more uniquely characterized) single particles prepared from gas phase.

Since the advantage of the single particle approach lies in the removal of the inhomogeneous broadening of the emission bands, we extended our efforts to make the detection of single gas phase prepared nanocrystals feasible. Finally we succeeded and concentrated both on the spectral characterisation of single silicon nanoparticles and the comparison of PL dynamics from differently prepared samples.

3.5.1 Photoluminescence dynamics

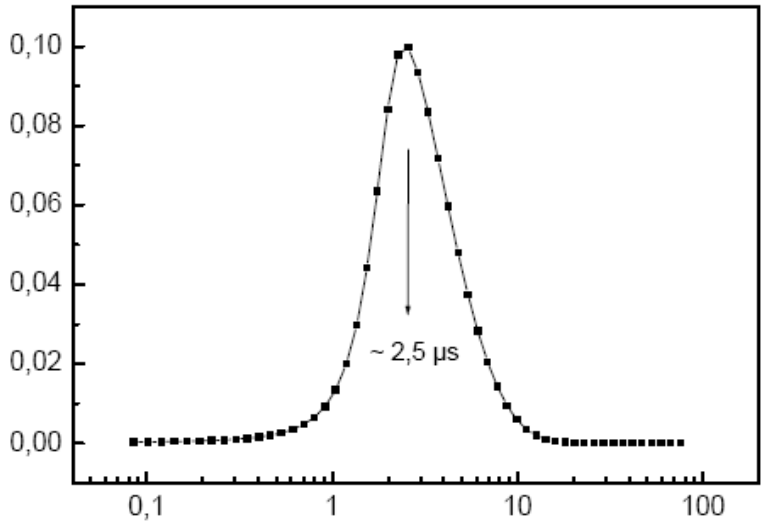

Fig. 1: Lifetime distribution of a non-size selected sample of gase-phase prepared silicon nanocrystals

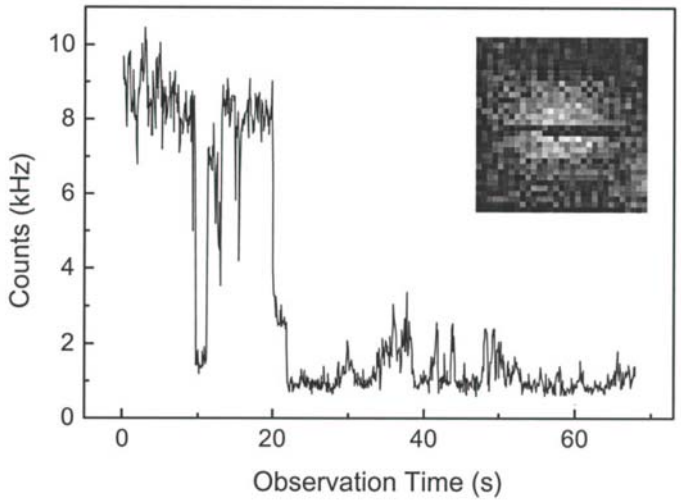

Fig. 2: PL blinking of a single porous silicon nanocrystal. The insert shows a confocal image of PL with black strips (off-times).

Ensemble PL of all type of silicon nanocrystals shows strong non-exponential decay dynamics as is shown in Fig. 1. This is usually attributed to the remaining size distribution relating each size to an individual decay rate. It is assumed that the main reason for this inhomogeneity is related to the (forbidden) indirect band gap transition of silicon which becomes modified by the size dependent quantum confinement. Whether this is indeed the only reason for the experimentally observed rate distribution is a not yet definitely answered question since experiments on other types of semiconductor nanocrystals such as CdSe (Fischer 2004) have shown that even for single nanocrystals the PL decay rate varies during the experimental observation time. Related phenomena are charging processes of the nanocrystals. For this reason we continued our experiments on photoinduced dynamics, which are also relevant in the astrophysical context, on silicon nanocrystals both on the single particle as on the ensemble level.

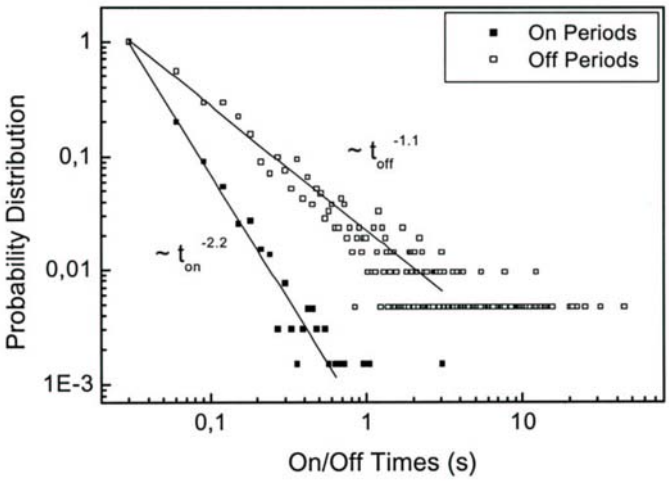

Fig. 3: Probability distribution of on- and off-times for one single porous silicon nanocrystal. The fits show a power law distribution.

Photoluminescence intermittency

As has already been reported in the previous report PL of single silicon nanocrystals turns "on" and "off" on time scales of ms and shorter (which is, however, not detectable due to our time resolution of about 10 ms and longer). A typical example is shown in Fig. 2 for a single nanocrystal from porous silicon. The figure shows PL intensity fluctuations which are also seen as "dark" or "bright" stripes during a confocal scan across the image of a nanocrystal. Counting dark (off) and bright (on) periods in a statistical manor results in probability distributions as is shown in Fig. 3 for a single nanocrystal and in Fig. 4 for 100 different nanocrystals. In both cases the statistics follow a power law $P \sim t^{-\alpha}$ behaviour with $\alpha \approx 2.2$ for the "on"-times and $\alpha \approx 1.2$ for the "off"-times. However, Fig. 5 shows while following the statics for single particles separately that there is broad distribution for α. Figs. 3 and 4 also reveal that time scales may definitely reach times of less than 100 µs. From this we conclude that these blinking dynamics might be also part of the decay dynamics collected in Fig. 1.

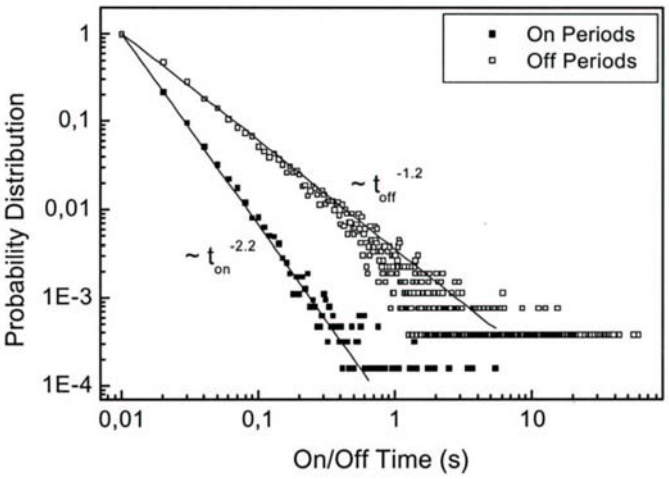

Fig. 4: Probability distribution of on- and off-times for 100 single porous silicon nanocrystals. The fits show a power law distribution.

Blinking dynamics have also been observed for other quantum systems such as colloidal semiconductors (Issac 2005) or organic molecules (Schuster 2005) with power law exponents α between 1 and 2. During the last years strong evidence has been provided (Issac 2005, Schuster 2005) that the reason for blinking dynamics is the charging of the quantum systems which is accompanied by a photoejection of the electron of the exciton, followed by a long-lived electron self-trapped in the dielectric environment. In the recently reported systems, this self-trapping depends on the dielectric constant of the embedding matrix. Contrary to the experiments on those systems, we did not observe a dependence of α on the dielectric properties of the environment, which we varied from quartz to PMMA. This might be related to the fact that the diameter of the SiO_2 shell is much larger than 1 nm which is at least the case for most of the porous nanoparticles (see Fig. 6). TEM reveals that the particle size is on average larger than 20 nm, while the experimentally observed PL is related to Si-core diameters smaller

than d = 10 nm. From this we conclude that electron trapping occurs in the (amorphous) SiO_2 shell or at the Si/SiO_2 interface.

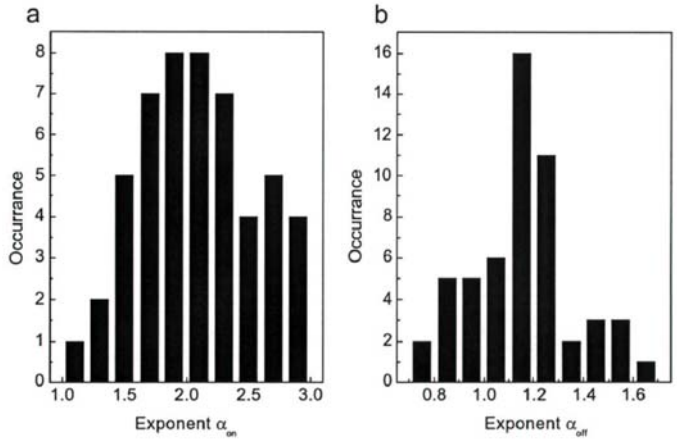

Fig. 5: Probability histrogram finding a certain power law exponent for the on-times (a) and the off-times (b).

Comparing the power law exponents reveals that $\alpha_{on} > \alpha_{off}$ which is similar to the blinking behaviour of molecules (Schuster 2005) but different from CdSe/ZnS where we observed nearly independent of the crystalline size that $\alpha_{on} \leq \alpha_{off}$ (Issac 2005).

A comparison of the results of different model calculations with experiments suggests that more than one process is involved in the formation of the dark state. Details of this comparison can be found in Ref. (Cichos 2004a).

Photoluminescence bleaching and recovery

A consequence of the blinking experiments on single nanocrystals with $\alpha_{off} < 1.5$ is, that with increasing observation times the "off" periods increase continuously. This corresponds to a so called "statistical aging". It should also be manifested in ensemble experiments. As we have already mentioned in the previous report, PL spectra decay in time scales of seconds and PL is shifted to the red upon continuous photoexcitation. However, blinking experiments suggest, that this might not be a permanent photobleaching but that at least part of the PL intensity is recovered after sufficient long waiting periods while keeping the sample in the dark.

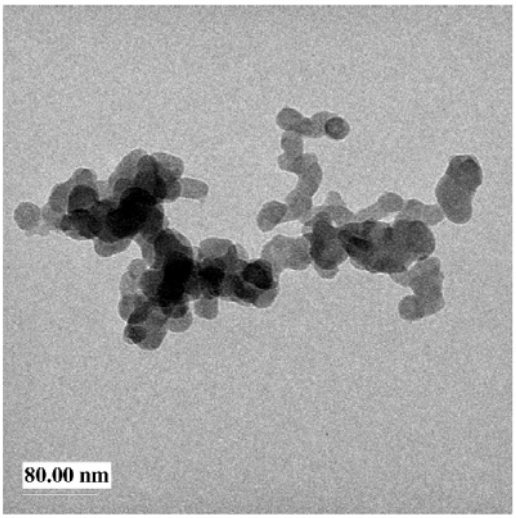

Fig. 6: TEM of porous silicon with silicon oxide shells. (Electron Micoscopy Laboratory, Prof. Hietschold , TU Chemnitz)

In fact, this can be experimentally observed as is shown in Fig. 7. After switching the exciting laser on, the PL intensity of a silicon ensemble decreases on time scales of seconds. After waiting in the dark the intensity is recovered. We have performed Monte Carlo simulations (for details see Ref. (Cichos 2004b) for the bleaching and recovery for different power law distributions (see Fig. 8) and compared it to the experimental data in Fig. 7. We were able to predict the bleaching and emission recovery of nanocrystal ensembles from the blinking statistics of single crystals and vice versa. This provides an additional tool to study nanocrystal blinking

behaviour especially at long times, where it is difficult to obtain sufficiently good statistics. Our results indicate that while waiting in the dark at least 80 % of the bleached PL can be recoverd. The close relationship between bleaching and PL intermittency is also demonstrated in Fig. 9 where the decay (bleaching) is compared with the sum of individual blinking traces normalized to the same initial intensity.

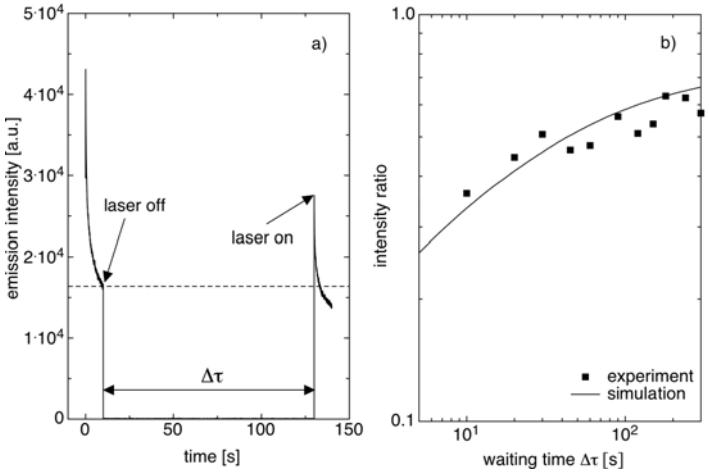

Fig. 7: (a) PL intensity as a function of laser irradiation time. (b) Ratio of PL intensity after switching the laser on to the intensity before switching off as a function of waiting time in the dark. The line shows a simulation with $\alpha = 1.7$ (see Fig 8).

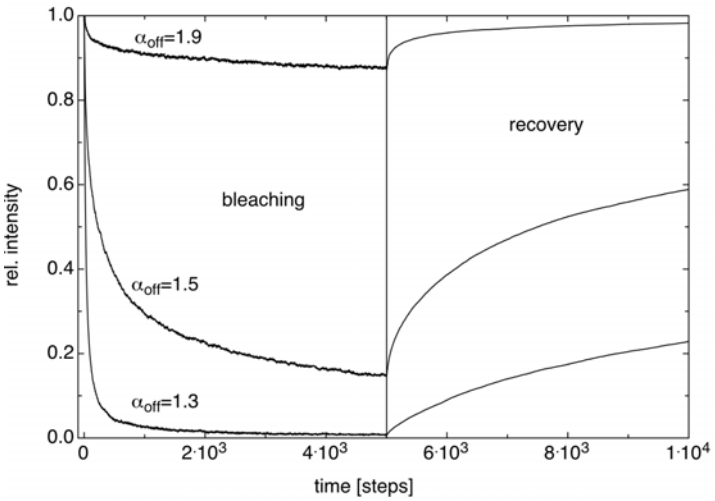

Fig. 8: Simulated bleaching and recovery curves for an ensemble of nanocrystals with different power law distributions for the off times.

These qualitative results are also of astrophysical relevance, since occurently happening photobleaching will not destroy PL for long times but will result in a PL recovery after sufficient long waiting times.

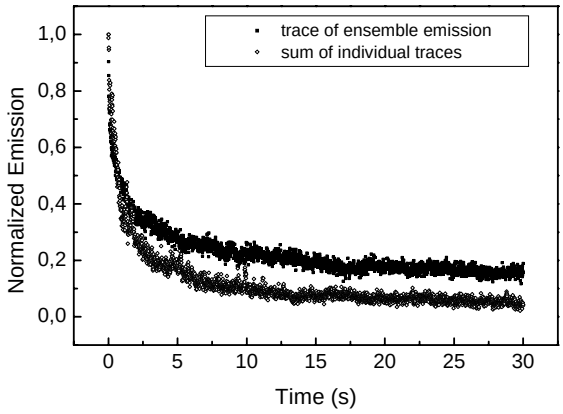

Fig. 9: Comparison between bleaching behaviour of an ensemble of gas-phase produced silicon crystals and the sum of 100 emission traces of single porous particles.

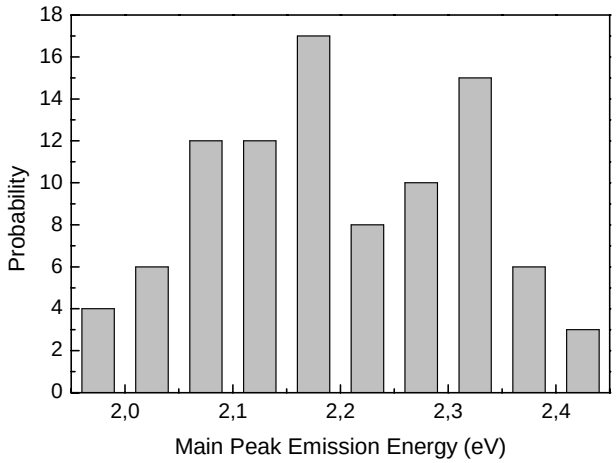

Fig. 10: Experimental probability to detect a singe silicon nanocrystal as prepared from gas-phase with laser excitation at 2.54 eV.

3.5.2 Spectroscopy on single silicon nanocrystals

Already in the previous report we have shown the feasibility to obtain PL spectra of at that time single porous silicon nanocrystals. We have extended these experiments and were now able to perform also spectroscopy on single crystals prepared in the gas phase.

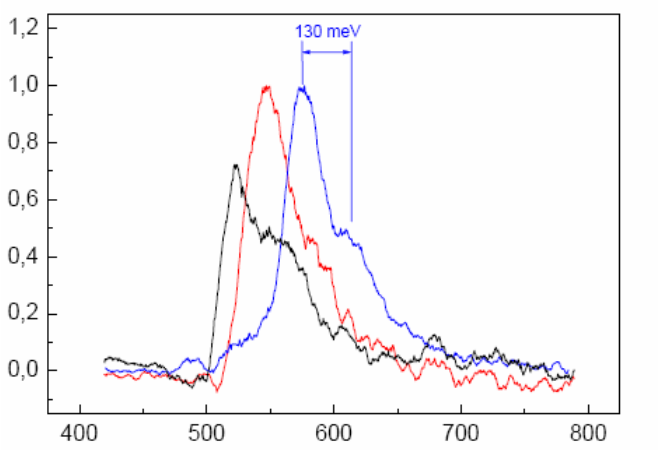

Fig. 11: Wavelength (in nm) PL spectra of 3 single porous silicon nanoparticles on a quartz substrate.

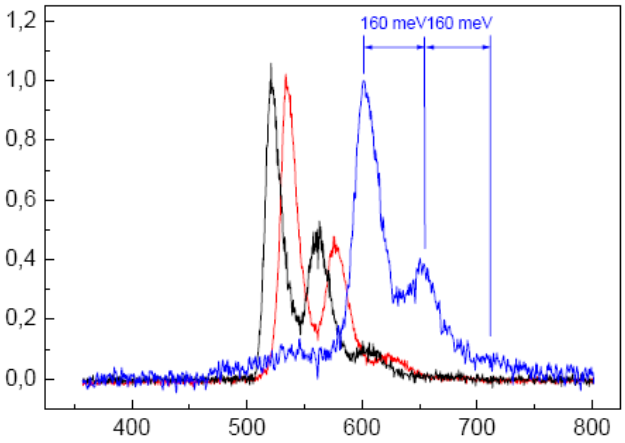

Fig. 12: Wavelength (in nm) PL spectra of 3 single porous silicon nanoparticles embedded in a PMMA matrix on a quartz substrate.

However, as Fig. 10 reveals, the spectral range in which we were able to detect silicon nanocrystals is limited to an energy range between about 1.9 and 2.45 eV. While the upper bound might be explained by a combination of the decreasing number of very small particles and the fixed excitation energy of 2.54 eV, the lower bound contradicts the range of PL observed in ensemble experiments. Presently this discrepancy is not completely understood but may be related to the increasing (radiative) decay rate (Huisken 2002) while decreasing the size of the nanocrystals.

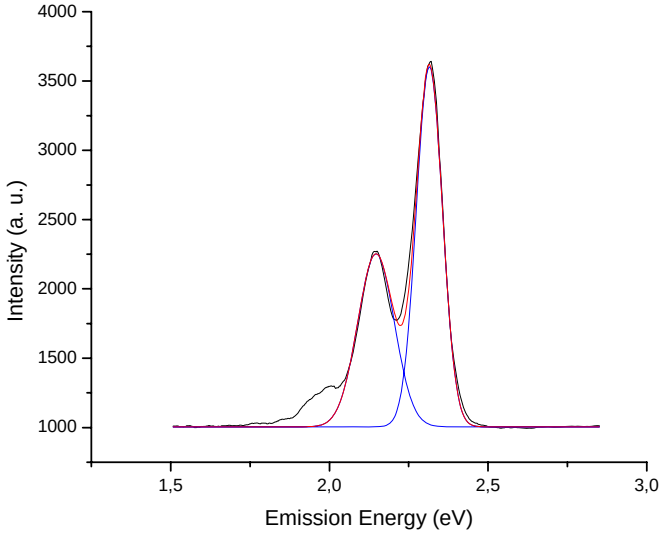

Fig. 13: PL energy of 1 single gas-phase prepared silicon nanoparticle on a quartz substrate. The zero phonon line and the phonon side band have been fitted by two Gaussian lines.

Figs. 11 – 13 show a selection of PL spectra under various conditions. They all have in common, that besides a (zero phonon) band at high PL energies additional bands are observed at lower energies, which are separated from the first band by energies corresponding to about 130 – 160 meV or multiples of these values. Since these splittings are too large to be related to Si phonons we assign them to SiO_2 vibrations of the SiO_2 shell. Corresponding TO- and LO-vibrations have been determined to be close to these values (Sa`ar 2005). However, a comparison of many spectra of single crystals reveals that these frequencies vary from crystal to crystal and seem also to depend on the crystal preparation or embedding matrix. Even crystals of - according to the PL energy - same size have different dynamic and static properties.

We like to make the point again that we could observe single crystal spectra only over a limited PL range, which – according to quantum confinement models- belongs to Si core diameters between 2 nm and 3 nm. This corresponds to the small diameter range of the size distribution, where we might expect an increased leaking of the excited wave function into the SiO_2 shell. We therefore have investigated the corresponding electron-phon coupling following concepts adapted from solid state spectroscopy.

3.5.3 Electron-phonon-coupling

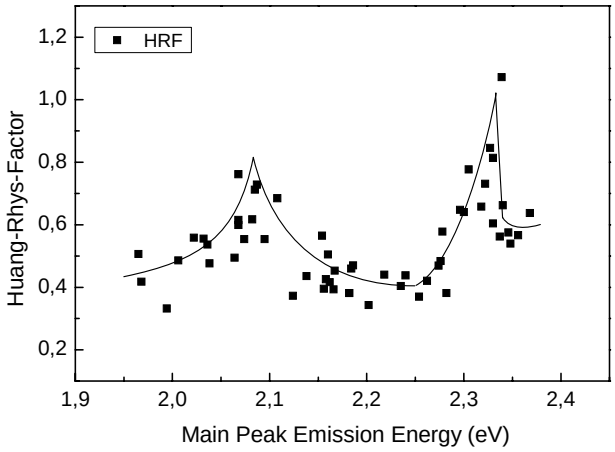

Fig. 14: Huang-Rhys Factor S as a function of PL energy of the zero phonon transition of gas-phase prepared single silicon nanoparticles.

For a series of spectra of gas phase prepared single crystals we have determined the electron-phon coupling as a function of PL energy. A common way to parameterize the coupling is to determine the Huang-Rhys factor S, which corresponds to the intensity ratio of the first phonon band to the zero phonon band. The results are shown in Fig. 14. Surprisingly, the Huang-Rhys factor S shows two peaks, which are clearly above the experimental error and close to the maxima of the distribution of particles which has been presented in Fig. 10. Presently we do not have a unique interpretation of the results. But strong evidence is provided that the observed phenomena are related to the localisation of the exciton from the initially excited silicon core into surface or trap states. Related observations have been recently reported (Wolkin 2002, Garrido 2004). Moreover, the similar structure observed in the distribution of PL energies (Fig. 10) and in the distribution of S (Fig. 14) as a function of PL energy indicate that this localisation might occur stepwise, that is via an independent localisation of electron and hole at different PL energies (crystal sizes).

3.5.4 Comparison of various silicon nanocrystals

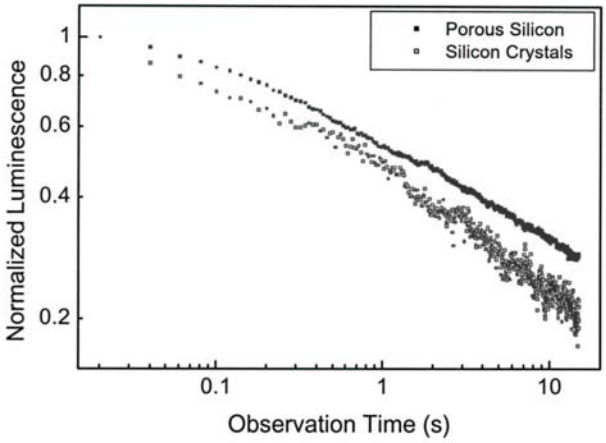

Fig. 15: PL intensity as a function of laser irradiation time of a silicon porous layer (top) and silicon from gas-phase preparation (bottom).

Our experiments have shown that independent of the preparation technique silicon nanocrystals exhibit comparable behaviour both with respect to spectral (see 3.5.2) and dynamic (see 3.5.1) properties.

Despite the differences in core/shell relations both types are obviously subject to very similar photodynamics which are (as can be also seen from Fig. 15) quite similar. Despite the fact that the preparation of porous silicon is a not very well defined chemical procedure and has often risen doubts about features reported

for such type of materials our results demonstrate that porous silicon crystals are suitable model compounds to describe silicon nanocrystals.

3.6 Zusammenfassung und Ausblick / Summary and future

In the last period we have collected and modelled photoluminescence dynamics and PL spectra for two types of differently prepared silicon nanocrystals. A comparison shows that there are no principal differences among these two systems. Over a limited range of PL energies silicon nanoparticles could be detected on the single particle level. Comparison of the photodynamics of single particles (blinking) and ensemble (bleaching) showed that with respect to dynamics both ensemble and single particle are subject to generally the same photoinduced processes. These processes are probably also present in interstellar space and might explain the persistence and spectral distribution of ERE emission, since in silicon nanoparticles photoinduced PL quenching is a reversible process being more effective at short PL wavelengths (small particles).

With respect to the spectroscopic behaviour we could only investigate silicon particles above PL energies of 1.9 eV, where we could detect an energy (size) dependent electron-phon coupling to interface vibrations, which is probably accompanied by a step-wise localisation of the exciton.

To investigate the processes at the interface in more detail, we suggest to continue experiments at low temperatures in order to increase spectral resolution. Although intended in the present period we were not able to address this question, since the determination of the electron-phonon coupling turned out be quite time consuming. Furthermore, a detailed investigation of PL lifetimes on the single particle level will provide more insight into the relation of radiative/non-radiative decay channels.

With respect to astrophysical relevance of silicon nanoparticles we suggest excitation wavelength dependent bleaching experiment at various temperatures in order to provide insight into the PL wavelength dependence of ERE with respect to the spatial proximity of various stellar radiation sources.

3.7 Literatur / References

Cichos, F., Martin, J., von Borczyskowski, C.: *Characterizing the non-stationary blinking of silicon nanocrystals*, J. Luminesc. **107** (2004a) 160-165.

Cichos, F., Martin, J., von Borczyskowski, C.: *Emission intermittency in silicon nanocrystals*, Phys. Rev. B **70** (2004b) 1153141- 11543149.

Fischer, B.R., Eisler, H.-J., Stott, V.E., Bawendi, M.G.: *Emission intensity dependence and single-exponential behaviour in single colloidal quantum dot fluorescence lifetimes*, J. Phys. Chem. B **108** (2004) 143-148.

Garrido, B.; López, M.; Pérez-Rodrígez, A.; García, C.; Pellegrino, P.; Ferré, R. Moreno, J. A.; Morante, J. R.; Bonafos, C.; Carrada, M.; Claverie, A.; de la Torre, J.; Souif, A. *Optical and electrical properties of Si-nanocrystals ion beam synthesezed in* SiO_2 , Nucl. Instr. Meth. B. **216** (2004) 213-221.

Heitmann, J., Müller, F., Yi, L., Zacharias, M. Kovalev, D., Eichhorn, F.: *Excitons in Si nanocrystals: Confinement and migration effects*, Phys. Rev. B **69** (2004) 1953091-7.

Huisken, F., Ledoux, G., Guillois, O., Reynaud, L.: *Light-emitting silicon nanocrystals from laser pyrolisis*, Adv. Mater. **14** (2002) 1861-1865.

Issac, A., Cichos, F., von Borczyskowski, C.: *Correlation between photoluminescence intermittancy of CdSe quantum dots and self-trapped states in dielectric media*, Phys. Rev. B **71** (2005) 1613021-1613024 (R).

Ledoux, G., Guillois, O., Huisken, F., Kohn, B., Porterat, D., Reynaud, C.: *Crystalline silicon nanoparticles as carriers for the Extended Red Emission*, Astron. Astro. Phys. **377** (2001) 707.

Martin, J., Cichos, F., Chan, I. Y., Huisken, F., von Borczyskowski, C.: *Photoinduced processes in silicon nanoparticles, Isr*. Journ. Chem. **44** (2004) 341-351

Martin, J., Cichos, F., von Borczyskowski, C.: *Spectroscopy of single silicon nanoparticles*, J. Luminesc. **108** (2004) 347-350.

Martin, J., Cichos, F., von Borczyskowski, C.: *Confocal microscopy of electrostatic properties of Si-quantum dots and silica surfaces by charge sensitive dye molecules*, Opt. Spectr. **99** (2005) 281- 288 and **99** (2005) 297-303.

Petrov, E.P., Cichos, F. , Zenkevich, E.I., Starukhin, D., von Borczyskowski, C.: *Time resolved photoluminescence anisotropy of CdSe/ZnS nanoparticles in toluene at room temperature*, Chem. Phys. Lett. **402** (2005) 233–238.

Petrov, E.P., Cichos, F., Spange, S., von Borczyskowski, C.: *Investigation of thetherable distilbazolium compounds as fluorescent probes in nanostructured silica sol-gel materials*, Photochem. Photobiol. **81** (2005) 898-907.

Petrov, E.P., Cichos, F., von Borczyskowski, C.: *Intrinsic photophysics of semiconductor nanocrystals in dielectric media: formation of surface states*, J. Luminesc. **119-120** (2006) 412-417.

Sa'ar, A.; Reichmann, Y.; Dovrat, M.; Krapf, D.; Jedrzejewski, J.; Balberg, I.: *Resonant coupling between surface vibrations and electronic states in silicon nanocrystals at the strong confinement regime*, Nan. Lett, **5** (2005) 2443-2447.

Schuster, J., Cichos, F., von Borczyskowski, C.: *Blinking of single dye molecules in various environments*, Opt. Spectr. **98** (2005) 712-717.

Schuster, J., Cichos, F., von Borczyskowski, C.: *Influence of self-trapped states and photoproducts on the intermittency of single molecules*, Appl. Phys. Lett. **87** (2005) 5195.

Schuster, J., Cichos, F., von Borczyskowski, C.: *Variation of power-law dynamics caused dark state recovery of single molecule fluorescence intermittency*, SPIE **6358** (2006) 6258041-8.

Schuster, J., Brabandt, J., von Borczyskowski, C.: *Discrimination of Photoblinking and Photobleaching on the Single Molecule Level*, J. Luminescence 2007, in print.

Shamirzaev, T.S., Gilinsky, A.M., Bakarov, A.K., Toropov, A.I., Tenne, D.A., Zhuravlev, K.S., von Borczyskowski, C., Zahn, D.R.T.: *Millisecond photoluminescence kinetics in a system of direct-bandgap InAs quantum dots in an AlAs matrix*, JETP Letters **77** (2003) 459-463.

Shamirzaev, T.S., Gilinsk, A.M., Toropov, A.I., Bakarov, A.K., Tenne, D.A., Zhuravlev, K.S., von Borczyskowski, C., Zahn, D.R.T.: *Model of Photoluminescence of InAs quantum dots embedded in dielectric band gap AlGaAs matrices*, Material Science (2004) 157- 1160.

Shamirzaev, T.S., Gilinsky, A.M., Toropov, A.I., Bakarov, A.K., Tenne, D.A., Zhuravlev, K.S., von Borczykowski, C., Zahn, D.R.T.: *Millisecond fluorescence in InAs quantum dots embedded in AlAs*, Physica E **20** (2004) 282-285.

Smith, Tracy L., Witt Adolf N.: *The photophysics of the carrier of extend red emission*, Astrophys. J. **565** (2002) 304-318.

Sychugov, I., Juhasz, R., Linnros, J., Valenta, J.: *Luminescence blinking of a Si quantum dot in a SiO2 shell*, Phys. Rev. B **71** (2005) 113331-5.

Tang, J., Macus, R.A.: *Diffusion-controlled electron transfer processes and power law statistics of fluorescence intermittency of nanoparticles*, Phys. Rev. Lett. **95** (2005) 107401.

von Borczyskowski, C., Cichos, F., Martin, J., Schuster, J., Isaac, A. Brabandt, J.: *Common luminescence fluctuations of singe particles and single molecules*, Europ. Phys. Journ. in print.

Witt, A. N., Gordon, K. D., and Furton D. G.: *Silicon nanoparticles as a source of extended red emission*, Astrophys. J. **501** (1998) L111-L115.

Witt, A.: *Observations of neutral and ionized PAM's in the red rectangle, Symp. On Interstellar Reactions*, Pillnitz (2005).

Wolkin, M. V., Jorne, J., Fauchet, P. M., Allan, G., Delerue, C.: *Electronic states and luminescence in porous silocon quantum dots: The role of oxygen*, Phys. Rev. Lett. **82** (1999) 197-200.

Zenkevich, E.I., Shulga, A.M., Petrov, E.P., Cichos, F., von Borczyskowski, C.: *Key-Hole principles and photochemistry of porphyrin self-organization on semiconductor quantum dots*, J. Porphyrins and Phthalocyanines **8** (2004) 4583.

Zenkevich, E.I., Shulga, A., Cichos, F., Petrov, E., Blaudeck, T., von Borczyskowski, C.: *Nanoassemblies designed from quantum dots and molecular arrays*, J. Phys. Chem. B **109** (2005) 8679-8692.

Zenkevich, E.I., von Borczyskowski, C.: *Structure and excited state relaxation dynamics in nanoscale self-assembled arrays: Multiporphyrin Complexes, Porphyrin-Quantum Dot Composites.*, SPIE **5849** (2005) 29-40.

Zenkevich, E.I.,, Shulga, A.M., Blaudeck, T., Cichos, F., von Borczyskowski, C.: *Competition in the formation of nanosize multiporphyrin complexes and porphyrin-quantum dot heterocomposites*, In: "Physics, Chemistry and Applications of Nanostructures. Reviews and Short Notes to Nanomeeting-2005" (V.I. Borisenko, S. V. Gaponenko, V. S. Gurin, Eds.), World Scientific Publishing Co., New Jersey, London, Singapore, Bejing, Shanghai, Hong-Kong, Taipei, Chennai. 367-370 (2005).

Zenkevich, E.I., von Borczyskowski, C.: *Photoinduced electron transfer and relaxation in selforganized multipohyrin nanoasssemblies* , In: "Fundamental Photoprocesses and Inhomogeneus Broadening of Electronic Spectra of Organic Molecules in Solution", Ed. V.I. Tomin, Slupsk (2006).

Zenkevich, E.I., Blaudeck, T., Shulga, A.M., Cichos, F., von Borczyskowski, C.: *Identification and assignment of porphyrin-CdSe hetero-nanoassemblies*, J. Luminesc. **122-123** (2007) 784-788.

Zenkevich, E.I., Shulga, A., Blaudeck, T., von Borczyskowski, C.: *Fabrication and primary photoevents in self-assembled nanocomposites on semiconductor quantum dots and tetrapyrrole Chromophores*, SPIE, in print.

Zenkevich, E.I. , Blaudeck, T., Abdel-Mottaleb, M., Cichos, F., Shulga, A.M., von Borczyskowski, C.: *Photophysical properties of self-aggregated porphyrin-semiconductor nanoassemblies*, Int. Journ. Photoenergy, in print.