

Plasma synthesis of group IV quantum dots for luminescence and photovoltaic applications*

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Abstract: The unique ability of nonthermal plasmas to form high-quality nanocrystals (NCs) of covalently bonded semiconductors, including the group IV elements silicon (Si) and germanium (Ge), has been extensively demonstrated over the past few years. Recently, plasma processing was also extended to the surface functionalization of NCs, imparting further functionalities to plasma-produced NCs such as solution-processability or the passivation of electronic surface states. This paper focuses on the synthesis and surface functionalization of Si- and Ge-NCs, and on their application in luminescent and photovoltaic devices.

Keywords: quantum dots; nonthermal plasmas; nanocrystals; solution-processability; passivation; group IV elements; photovoltaics.

INTRODUCTION

Nanoparticle formation in plasmas has been known for decades, however, it was mainly considered a nuisance leading to contamination problems during plasma processing [1,2]. Correspondingly, nanoparticle formation was unappreciatively termed “dust” formation and nanoparticle-containing plasmas were referred to as “dusty plasmas” [3]. While large efforts were made to control and avoid dust formation in plasmas, some first reports of harnessing the properties of plasmas for the controlled synthesis of nanocrystals (NCs) to improve the properties of materials [4] or for use in novel devices [5] started to emerge in the late 1990s.

Largely unnoticed by the plasma community, research in the NC community focused on the new and exciting properties of quantum confined semiconductor nanoparticles, whose dimensions are on the order of or smaller than the Bohr exciton radius of the material [6,7]. Among some of these exciting new properties are the size-tunable optical properties of NCs [8], the high electrical conductivities achieved in thin films of interacting NCs [9,10], and the formation of multiple excitons (bound electron-hole pairs) in response to absorption of a single photon [11–13], an effect that may lead to NC solar cells with enhanced efficiencies. Interestingly, a survey of the NC literature reveals that the vast majority of studies in this field have been conducted on II–VI and IV–VI chalcogenide semiconductors, for which convenient wet-chemical synthesis routes in colloidal solutions are well established. Noticeably (largely) absent are studies of group IV and many of the III–V semiconductor NCs, which due to their

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stronger covalent bonding and accordingly higher melting points are very difficult to produce in solution. However, compared to the II–VI and IV–VI semiconductors, which often contain toxic heavy metals, particularly the group IV semiconductors have the advantages of being nontoxic, environmentally benign, stable, and abundant.

Over the past few years, we and others have demonstrated that low-pressure plasmas are interesting sources for the controlled synthesis of NCs of group IV [14–16] and III–V [17] materials. As such, plasma NC synthesis can fill an important gap in the universe of available NC materials. While many of the group IV and III–V materials could be synthesized with other gas-phase synthetic routes such as thermal pyrolysis [18] or laser pyrolysis [19], plasma synthesis has some unique advantages compared to other gas-phase methods: (1) The negative charging of nanoparticles in plasmas leads to their mutual electrostatic repulsion, allowing for the synthesis of nonagglomerated particles. In other gas-phase approaches, particles are essentially uncharged and agglomeration can only be avoided by strongly reducing the particle concentration, making them unsuitable for large-throughput processing. (2) Strongly exothermic surface reactions combined with slow heat transfer at low pressures result in particle temperatures which can exceed the gas temperature by hundreds of Kelvin [15,20]. These conditions are ideal for the synthesis of high-quality crystals of high melting point materials and particularly covalently bonded semiconductors.

In this paper, we briefly describe the principle of plasma synthesis of semiconductor NCs, the utilization of plasmas to NC surface functionalization, and applications of these materials in luminescent and photovoltaic devices.

NANOCRYSTAL SYNTHESIS

Si- and Ge-NCs are synthesized in a radio-frequency (RF) flow-through reactor. A plasma is excited in a cylindrical quartz tube by applying 50–100 W of RF power to a set of ring electrodes (Fig. 1a, upper plasma). The inner diameter of the quartz tube typically ranges between 6–25 mm, and the length of the plasma zone is 3–6 cm. The particle precursor is flown through the tube in an argon buffer gas. The residence time of the gas in the plasma zone is on the order of 2–20 ms and determines the NC size. Si crystals are synthesized from silane, Ge crystals from a Ge tetrachloride/hydrogen mixture. After the

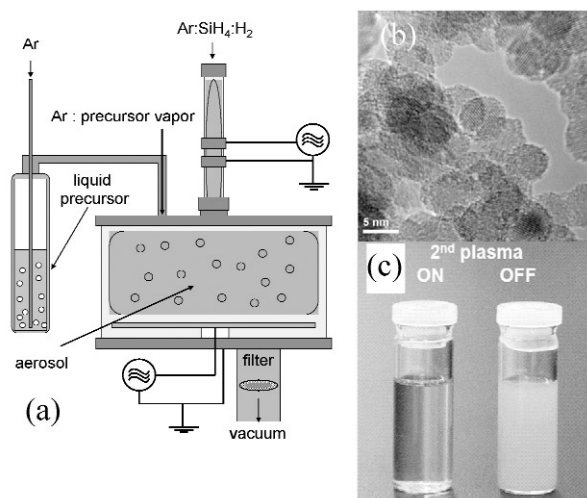


Fig. 1 (a) Scheme of the dual plasma for the synthesis (upper plasma) and functionalization (lower plasma) of Si-NCs; (b) TEM image of Si-NCs; (c) effect of Si-NC surface functionalization in 2nd plasma.

synthesis, NCs are extracted from the reactor by the gas flow and deposited on various kinds of substrates for characterization, or collected on filter meshes for further processing.

The electrostatic repulsion between particles enables synthesizing nonagglomerated Si- and Ge-NCs at high mass yields. For instance, with a simple flow reactor consisting of a 6 mm inner diameter glass tube, up to 50 mg/h of luminescent Si crystals can be synthesized [15].

NCs are characterized with various techniques. Fourier transform infrared spectroscopy is used to study the surface conditions of the NCs. It is found that NCs have hydrogen-covered surfaces. When exposed to air, a ~1 nm thick layer of Si oxide forms over several days. Transmission electron microscopy (TEM) (Fig. 1b) and X-ray diffraction are used to study the NC microstructure. We find that the nanoparticles are virtually 100 % crystalline, and that their size distribution is highly monodisperse with a standard deviation of ~15 % of the average size.

NANOCRYSTAL FUNCTIONALIZATION

NC surface functionalization can serve different purposes such as making NCs soluble in a range of solvents to make them solution-processable, or passivating electronic surface states, which may give rise to nonradiative recombination processes in luminescent NCs.

A range of surface functionalization schemes have been developed by our group. In one approach, NCs are collected as a powder, transferred under exclusion of oxygen into a liquid phase reactor (Schlenk line), and a reaction scheme known as hydrosilylation [21] is performed under dry nitrogen. This reaction has widely been used for flat Si wafers [21] as well as for Si particles [22,23]. In this thermally initiated reaction, alkenes or alkynes bond with a hydrogen passivated Si surface via a free-radical mechanism. In our experiments, octadecene- or dodecene-capped particles were prepared by dispersing particles in a mixture of 1 part octadecene (or dodecene) in 20 parts mesitylene as a solvent. After approximately 1 h of reaction time at 165 °C, the solution became clear, indicating that initial agglomerates of Si-NCs were broken up and that a stable colloidal solution was formed. The reaction was maintained under reflux conditions for another few hours to insure complete surface termination.

Si-NCs treated in this way exhibit optical properties which are strongly modified from the bulk material. Si in its bulk form belongs to the group indirect bandgap semiconductors, which are notoriously poor optical emitters and absorbers since radiative processes require the interaction with momentum-balancing phonons. This is evidenced by the fact that the quantum yield for photoluminescence (PL), defined as the ratio of emitted photons to absorbed photons, for bulk Si is close to zero (about 10^{-6}). However, for organically functionalized Si-NCs, we could demonstrate PL quantum yields as high as 60–70 % [24,25], which, for the first time, rival those of the direct bandgap II–VI semiconductor NCs.

Quite often, a virtually complete surface coverage with organic ligands is not required, for instance, in cases where one is just interested in making NCs solution-processable. In such cases, we recently demonstrated that plasmas offer an interesting route to fast surface functionalization through plasma-activated grafting of organic molecules onto NC surfaces [26]. This scheme is based on a dual-plasma approach in which NCs are synthesized in a first synthesis reactor, and immediately injected into a second reactor, in which a vapor of an organic precursor is activated and grafted onto the NC surfaces (Fig. 1a). In the case of Si-NCs, we could demonstrate that the organically passivated particles collected downstream of the second plasma readily go into solution in nonpolar solvents to form Si-NC “inks” (Fig. 1c). The PL quantum yield of these NC inks is smaller than that of liquid-phase processed Si-NCs, which suggests that the surface conditions of liquid-phase and plasma-functionalized NCs are different. However, the fact that plasma-functionalization proceeds on time scales of less than 1 s while liquid-phase functionalization takes several hours demonstrates the significant advantage of this approach for many applications.

LUMINESCENT APPLICATIONS

Significant progress has been made in recent years in the areas of high-efficiency solid-state light sources, largely based on InGaN technology [27]. Many of these applications rely on epitaxially grown thin film materials. However, in the areas of flexible displays and possibly electrically pumped lasers compatible with CMOS chip technology [28], there appears to be room for NC-based light-emitting devices.

Si-NC electroluminescence has been demonstrated from Si crystals dispersed in various dielectric matrices [29]. However, these devices rely on excitons formed by high field effects and are therefore inherently limited to low quantum efficiency Si-NC emission.

In one approach to enhance carrier transport to the Si-NCs, thereby increasing the potential quantum efficiency, we randomly dispersed surface-oxidized Si-NCs (Si/SiO₂ NCs) within the conductive polymer poly(9-vinylcarbazole) (PVK) [30]. The PVK(Si/SiO₂) hybrid devices produced simultaneous emission from PVK and Si/SiO₂ NCs (Fig. 2). Based on device energetics, four different energy transfer (ET) mechanisms may be responsible for producing the observed Si/SiO₂ NC emission. The dominant ET mechanism was determined by varying the π -conjugation to Si/SiO₂ NC spatial separation using poly(flourene) (PFE) polymers. The PFE alkyl side chains were chosen to impose known spatial separations that affect the ET processes occurring between the polymer π -conjugation and Si/SiO₂ NCs. No Si/SiO₂ NC emission was observed from the PFE hybrid devices, independent of the side chain length. These results suggest that the observed Si/SiO₂ NC emission from PVK(Si/SiO₂) hybrid devices is produced by direct carrier injection.

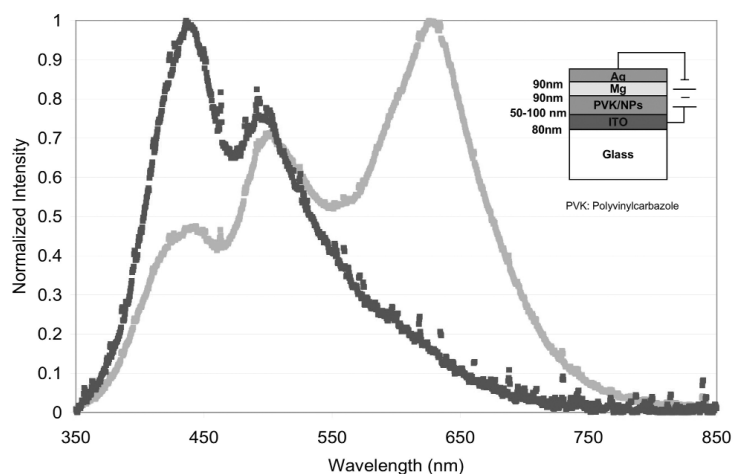


Fig. 2 Schematic and electroluminescence spectrum of a hybrid PVK Si-NC light-emitting device.

PHOTOVOLTAIC APPLICATIONS

For photovoltaic applications, the size-tunable bandgap of the NCs is of particular interest. Through optical emission spectroscopy we confirmed that the bandgap of Si crystals can be tuned between 1.1–2.0 eV by changing the NC size [24]. Equally, the bandgap of Ge crystals can be changed between 0.66–1.1 eV. Moreover, with material synthesized with the above plasma approach, multi-exciton generation in Si-NCs was for the first time observed in [31].

One possible route of utilizing NCs in photovoltaic cells is to use them as starting material for gas-phase or solution-processed thin films. If ways can be devised to form high-conductivity films of interacting but not touching NCs, quantum confinement may be used to adjust the bandgap of the material just by changing the NC size. Different techniques have been used by our group to form NC films.

Colloidal NCs can be coated onto substrates from solution via dip-, drop-, or spin-coating. Evaporation of the solvent leads to densely packed NC layers. These films are initially highly resistive. However, heating of the films to 300–400 °C seems to remove the majority of the organic ligands and the film conductivity increases.

In a different approach, NCs can be deposited directly from the gas phase without prior functionalization with organic ligands. For instance, films of Ge-NCs were deposited on 1737 Corning glass substrates lithographically patterned with aluminum (Al) electrodes for co-planar conductivity measurements. Three sets of electrodes—with interelectrode spacings of 5, 10, and 100 μm —are on each substrate, and current–voltage (I – V) characteristics are measured across these contacts both in the dark and under simulated air-mass (AM) 1.5 solar irradiation.

As shown in Fig. 3, as-deposited Ge-NC films show negligible conductance both in the dark and under AM 1.5 light, regardless of the deposition time. However, films that are subjected to a 10 min, 100 °C anneal in a nitrogen environment prior to air exposure exhibit conductivities that are photo-sensitive, field-dependent, and surprisingly large. The annealing step must be done in an inert environment to avoid accelerating the Ge-NC oxidation process that is discussed below. The effect of annealing is not yet understood. TEM studies of Ge-NCs prepared and annealed under identical conditions have shown that physical changes such as coalescence of neighboring particles do not occur for temperatures lower than 250 °C. Changes in the surface chemistry of the NCs may therefore be responsible for the observed change in conductivity.

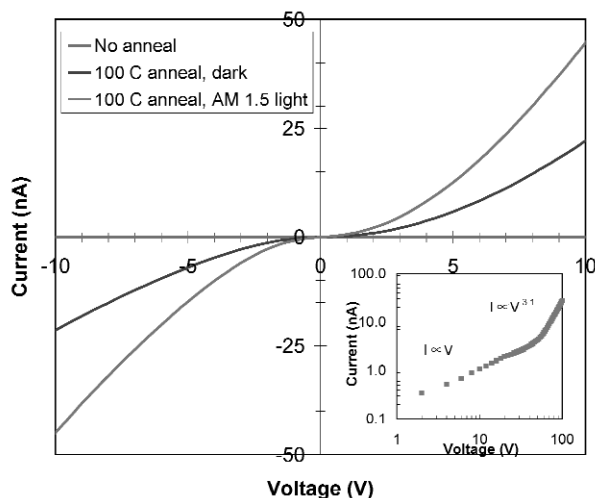


Fig. 3 I – V characteristics of annealed and unannealed samples deposited for 60 min. Inset: Log–log plot of a sample deposited for 10 min showing two distinct power law regimes.

When plotted on a log–log scale, the I – V characteristics linearize, and two distinct regions are observed (Fig. 3, inset). At low voltages, Ohmic behavior is seen, while above some onset voltage which varies from sample to sample, the current has a power law dependence on the applied bias where the power is always 2 or greater. Such behavior is characteristic of space-charge-limited (SCL) transport. The conductivity can be calculated using the slope of the Ohmic region of the characteristic, for which too few carriers have been injected into the film from the electrodes for SCL transport to begin. In the dark, conductivities as large as 10^{-7} S/cm have been measured for films deposited for 30 min, using film thicknesses as determined by cross-sectional scanning electron microscopy. Accounting for the large porosity of the films (roughly 99 % as determined by Rutherford backscattering) the conductivity intrinsic to the Ge-NCs—that is, the conductivity that would be calculated for a fully dense film of NCs—

is nearly two orders of magnitude larger. Under AM 1.5 light, the conductivity has been observed to increase by up to one order of magnitude, although a factor of 2–5 is more typical. Photosensitivity is particularly important for photovoltaic applications since it demonstrates that the Ge-NCs successfully absorb light and generate electron-hole pairs which can then be separated and collected. The light conductivity observed in our films approaches the light conductivity of hydrogenated amorphous Si films of $\sim 10^{-4} - 10^{-3}$ S/cm.

Yet another approach of using plasma-synthesized NCs relies on blending Si-NCs with conductive polymers in hybrid organic–inorganic devices. Conductive polymers are often good hole conductors, while percolating networks of Si- and Ge-NCs can function as electron conduction medium.

To form a hybrid solar cell, Si-NCs were dispersed in chloroform without further surface functionalization. A conjugated polymer, poly-3(hexylthiophene) (P3HT), was then dissolved in the chloroform solution which contained 5–8 nm Si-NCs. Thin-film hybrid solar cells were made by spin-coating the solution of P3HT and Si-NCs onto substrates pre-coated with poly(3,4-ethylenedioxy thiophene)/poly(styrenesulfonate) (PDOT:PSS) on indium tin oxide (ITO) on glass (Fig. 4). Al electrodes were evaporated on top of the P3HT/Si-NC film. Light is absorbed both by the P3HT polymer and the Si-NCs. Efficient exciton dissociation can be achieved at the interface of P3HT and Si-NCs due to the relative alignment of their energy bands.

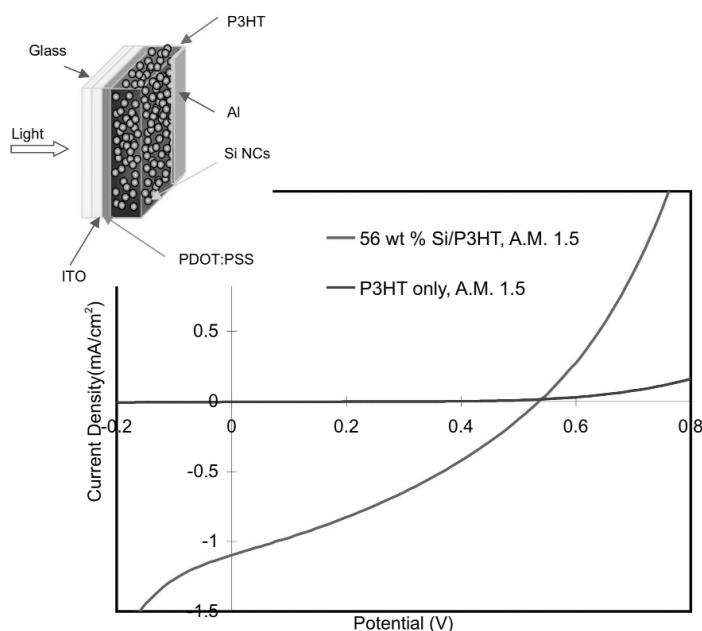


Fig. 4 Schematic and I–V characteristic of an Si-NC-P3HT hybrid solar cell.

Preliminary solar cells were made by spin-coating of solution of 50–70 % Si-NCs (by weight) in P3HT. Films of the Si-NC/P3HT blend were about 100 nm thick. First cells showed performances that leave room for improvement: Under AM 1.5 global solar conditions, short circuit current densities of >1 mA/cm² and open circuit voltages of ~ 0.55 V were achieved. Scanning electron microscope image analysis showed that Si-NCs form connected networks in the film, but are not uniformly distributed throughout the film. This non-uniform morphology is believed to decrease the efficiency of the solar cells. Work on improving the film morphology is in progress.

CONCLUSIONS

We have shown that nonthermal plasmas are attractive sources for the synthesis and surface functionalization of Si- and Ge-NCs. The approach can likely be extended to other covalently bonded semiconductors as well. Applications of Si- and Ge-NCs in luminescent and photovoltaic devices were demonstrated.

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