Space charge-limited current transport in thin films of alkyl-functionalized silicon nanocrystals

Simon Pfaehler\textsuperscript{1,7},\textcopyright\, Arzu Ang\textsuperscript{2,3,7},\textcopyright\, Domenikos Chryssikos\textsuperscript{4},\textcopyright\, Anna Cattani-Scholz\textsuperscript{4,5},\textcopyright\, Bernhard Rieger\textsuperscript{2,3} and Marc Tornow\textsuperscript{1,5,6}

\textsuperscript{1}Molecular Electronics, Technische Universität München, Theresienstr. 90, D-80333 München, Germany
\textsuperscript{2}WACKER-Lehrstuhl für Makromolekulare Chemie, Technische Universität München, Lichtenbergstr. 4, D-85747 Garching, Germany
\textsuperscript{3}Catalysis Research Center, Ernst-Otto-Fischer-Straße 1, D-85748 Garching, Germany
\textsuperscript{4}Walter Schottky Institut and Physics Department, Technische Universität München, Am Coulombwall 4, D-85748 Garching bei München, Germany
\textsuperscript{5}Center for NanoScience (CeNS), Ludwig-Maximilians-University, Geschwister-Scholl Platz 1, D-80539 Munich, Germany
\textsuperscript{6}Fraunhofer Research Institution for Microsystems and Solid State Technologies (EMFT), Hansastr. 27d, D-80686 München, Germany

E-mail: tornow@tum.de

Received 8 March 2019, revised 26 May 2019
Accepted for publication 24 June 2019
Published 15 July 2019

Abstract
We describe the fabrication and electrical characterization of all-silicon electrode devices to study the electronic properties of thin films of silicon nanocrystals (SiNCs). Planar, highly doped Si electrodes with contact separation of 200 nm were fabricated from silicon-on-insulator substrates, by combination of electron beam lithography and reactive ion etching. The gaps between the electrodes of height 110 nm were filled with thin-films of hexyl functionalized SiNCs (diameter 3 nm) from colloidal dispersions, via a pressure-transducing PDMS (polydimethylsiloxane) membrane. This novel approach allowed the formation of homogeneous SiNC films with precise control of their thickness in the range of 15–90 nm, practically without any voids or cracks. The measured conductance of the highly resistive SiNC films at high bias voltages up to 60 V scaled approximately linearly with gap width (5–50 μm) and gap filling height, with little device-to-device variance. We attribute the observed, pronounced hysteretic current–voltage (I–V) characteristics to space-charge-limited current transport, which—after about twenty cycles—eventually blocks the current almost completely. We propose our all-silicon device scheme and gap filling methodology as a platform to investigate charge transport in novel hybrid materials at the nanoscale, in particular in the high resistivity regime.

Supplementary material for this article is available online

Keywords: space charge-limited current transport, silicon nanocrystals, alkyl-functionalized, silicon electrodes, thin film, gap filling, PDMS membrane

(Some figures may appear in colour only in the online journal)

\textsuperscript{7} These authors contributed equally to this work.
1. Introduction

Semiconductor nanoparticles and nanocrystals (NCs) have gained much significance in electronics and optoelectronics, ranging from fundamental studies on the intriguing transport phenomena in NC arrays to applications in thin-film transistor devices, photovoltaic devices, LEDs, [1, 2] and as fluorescent labels [3]. Among the variety of semiconductor materials under investigation silicon has adopted a particular role due to its dominating relevance in microelectronics, its abundance and low toxicity [4]. Silicon nanocrystals (SiNCs) show distinct optical properties such as size-tunable photoluminescence (PL) in the visible range with high quantum yields when their size is reduced below the Bohr radius of Si \(d < 5 \text{ nm}\) [5–7]. For this reason, photoluminescent SiNCs have evolved as promising material for electronic and optoelectronic applications, including, e.g. (electro-)luminescent) synaptic devices [8, 9]. In order to prevent oxidation of the SiNCs surface as well as to control their electronic properties, a well-tailored surface functionalization is essential [10, 11]. Methods to synthesize SiNCs and functionalize their surfaces with a variety of different molecules are well developed [12, 13], as predominantly demonstrated in optical studies [14–16].

For electrical device applications covering for example novel (ultra) thin-film transistors, sensors or non-volatile memories, based on hybrid inorganic-organic 2D or 3D networks of functionalized SiNCs, the characterization and understanding of their electronic transport properties is mandatory [17, 18]. The group of Kortshagen has reported electrical data, mostly focusing on alkyl-functionalized, doped SiNC networks [19]. The systematic investigation of undoped SiNCs which are functionalized with aliphatic (electrically insulating) molecules poses a particular challenge on the experimental realization: (1) due to the high resistance of the SiNC films, the spacing between the electrical contacts needs to be small (100 nm regime), (2) the space between the contacts (gap) needs to be filled with the SiNC material in a controlled, homogeneous and reproducible manner, and (3) the electrode contact material has to be inert, both chemically and physically with respect to the high electric fields that need to be applied. This way, artifacts arising from, e.g. electromigration of metal ions from the contacts into the SiNC film [20] shall be excluded.

Here, we report on the electrical characterization of films of hexyl functionalized SiNCs (Hex-SiNCs, \(d \sim 3 \text{ nm}\)) [21], filled into 200 nm long and 110 nm high trench-like gaps, which separate pairs of degenerately doped Si contact electrodes (see figure 1(f), for the definition of the gap dimensions ‘width’ and ‘length’). Using a newly developed PDMS (polydimethylsiloxane) -based pressure technique related to solution micromolding fabrication processes [22], we achieved a high level of control over the film thickness within the trench, ranging from about 15–90 nm (almost complete filling). The obtained electrical transport data, carried out in the high voltage range up to 60 V, directly reveal the monotonic, practically linear dependence of current with respect to gap width and filling level. A pronounced hysteretic current–voltage \((I–V)\) characteristic points to a dominating space-charge-limited current transport mechanism in Hex-SiNC films. Our demonstrated Si electrode fabrication technique combined with the controlled gap filling method can serve as a platform for the electrical characterization of nm-thin films comprising different NCs passivated with various functional organic groups.

2. Experimental methods

The process of Si device fabrication and filling the active gap region between the contacts with a thin film of Hex-SiNCs is outlined in figure 1. Starting from a silicon-on-insulator (SOI) wafer with a highly doped top Si device layer (a), gap-separated electrodes were fabricated by using electron beam lithography (EBL) and reactive ion etching (RIE), after electrical contact metallization using conventional photolithography and physical vapor deposition (PVD) had been realized (b). At this stage, the device was ready to investigate the electrical properties of the material (here: Hex-SiNCs) to be filled into the gap—with the highly doped Si surfaces acting as electrical contacts in a two-terminal configuration [23–26]. We devoted much effort to the controlled and reproducible filling of the gap with SiNCs. Few procedures have been reported in literature, demonstrating the filling of (metallic) nanoscale trenches by different approaches [27, 28]. We tried several alternative methods, such as spin coating, drop casting or solvent evaporation to fill the gaps. However, none of these techniques led to satisfying filling with a homogeneous thin film of SiNCs. By far, the best results were obtained by mechanically pressing the SiNCs from solution into the gap, employing a pressure-transducing PDMS membrane (see figures 1(c)–(e)). This novel approach, particularly developed for this purpose, turned out to enable the formation of homogeneous Hex-SiNC thin films with precise control of thickness, practically without any voids or cracks in-between the Si electrodes. To achieve this, the native oxide on the Si electrode surface was first removed chemically by using hydrofluoric acid (HF). Immediately afterwards, a solution of Hex-SiNCs was drop-casted onto the chip surface (figure 1(c)) and mechanically pushed into the trench by application of a pressure-transducing PDMS membrane (d) which was subsequently removed (e). The final device structure featuring its gap filled with Hex-SiNCs was then ready for electrical characterization (f).

2.1. Preparative methods

2.1.1. Fabrication of silicon electrodes. Silicon electrodes were fabricated from SOI wafers (Soitec, France), composed of a \((110 \pm 7.5) \text{ nm}\) thin silicon device layer (100) separated by a \((200 \pm 5) \text{ nm}\) buried silicon dioxide \((\text{SiO}_2)\) layer from the silicon handle wafer (100). The top silicon layer was heavily p-doped by ion implantation \((p^+, \text{ Boron}, \text{ doping concentration ca } 5 \times 10^{19} \text{ cm}^{-3})\). The SOI wafers were diced
in 8 × 8 mm² sample chips. For the fabrication of an array of electrode pairs (figure SI1, available online at stacks.iop.org/NANO/30/395201/mmedia, supporting information), the SOI sample chips were first cleaned by sonicating them in acetone (VLSI Selectipur, BASF), subsequent sonicating them in isopropanol (VLSI Selectipur, BASF) and blowing them dry under a stream of N₂, followed by an additional cleaning step in oxygen plasma (180 s, 400 W). We used conventional photo-lithography to pattern the etching mask for the mesa-structure of the electrodes array: At first, an adhesion promoter hexamethyldisilazane (HMDS, Aldrich Chemistry) and a positive-tone photo resist (AZ5214E, MicroChemicals) were deposited by spin-coating (film thickness: 1.6 μm). Following resist development (AZ351B, 1:4 diluted with DI H₂O, MicroChemicals) and an additional oxygen plasma treatment to remove adhesion promoter and resist residues (180 s, 400 W), the mesa-structure was etched in the top silicon device layer down to the buried oxide by RIE (SF₆/C₄F₈ plasma, OXFORD Instruments, Plasma Lab 80 Plus). In that way, we produced an electrically conductive lead structure comprising an array of ten silicon layer bars of widths w ranging from 5 to 200 μm, which are electrically separated from each other and act as the basis for the later fabricated electrode arrays. After the RIE step, the remaining resist was removed in a subsequent ultrasonic bath of acetone, followed by rinsing in isopropanol and dry-blowing with N₂.

To provide ohmic contact to the highly doped Si lead structures we fabricated a row of Ti/Au metallic contact pads on top of the Si layer. These pads of area 200 × 200 μm² were prepared by a combination of photo-lithography (positive photo resist AZ5214E, MicroChemicals), a short dip in diluted HF (5%, 30 s) to remove the native oxide, and subsequent PVD of 10/100 nm Ti/Au (Leybold L560, max 0.2 nm s⁻¹), followed by lift-off in an acetone bath, rinsing in isopropanol and dry-blowing with N₂.

EBL was used to prepare the etching mask for gap fabrication. After cleaning the samples by sonicating in acetone (10 min), followed by sonicating them in isopropanol and dry-blowing with N₂, and an additional cleaning step in oxygen plasma (60 s, 400 W) the sample chips were coated with positive-tone EBL resist (80 nm, AR-P 6200, Altresist) and exposed in an EBL system (30 kV acceleration voltage, e_LINE, Raith). After developing (60 s, AR 600–546, Altresist) the samples were baked on a hotplate at 130 °C for 60 s to improve the etching stability of the EBL resist. The resulting resist gap pattern was transferred into the top Si layer by RIE as previously described, eventually resulting in gaps in the silicon mesa (see figure 1(b) and figure SI1, one between each pair of metal pads). In this way, each top silicon layer bar of the mesa was split in ten electrode pairs resulting in an array of 100 electrode pairs in total, on each sample. The remaining e-beam resist was removed by subsequent sonicatation in acetone and isopropanol plus the additional application of an oxygen plasma (5 min, 400 W).

2.1.2. Synthesis of hexyl functionalized SiNCs. Preparation of SiNCs embedded in SiO₂ like matrix started from the synthesis of polymeric hydrogen silsesquioxane (HSQ), based on a literature-known procedure [29]. To obtain free-standing hydride-terminated SiNCs, we applied a synthetic procedure which was recently described in detail [30].

Surface functionalization of the obtained SiNCs with hexyl groups was performed with organolithium reagents, as
we have reported before [21]. Freshly etched hydride-
terminated SiNCs (from 300 mg Si/SiO2 composite) were
dispersed in 2 ml dry toluene and transferred to a Schlenk
flask equipped with a stir bar. The dispersion was degassed
via three freeze-thaw cycles. n-hexyllithium (0.2 mmol, from
2.3 M solution in hexane) was added. Upon addition of n-
hexyllithium, the color of the reaction mixture turned dark
brown. The reaction mixture was stirred at room temperature
for 15 h under argon atmosphere. Functionalized SiNCs were
precipitated in 5 ml 1:1 ethanol–methanol mixture, acidified
with HCl conc. (0.2 ml) to terminate the reaction. SiNCs were
centrifuged at 9000 rpm for 5 min and the sediment was
redispersed in minimum amount of toluene. The precipitation-
centrifugation-redispersion cycle was repeated two more
times from toluene and ethanol-methanol. At the end of
purification steps, functionalized SiNCs were dispersed in
2 ml toluene and filtered through a 0.45 μm PTFE syringe
filter. This method assures a controlled, less dense monolayer
coverage on the SiNC surface, unlike many other conven-
tional surface functionalization techniques [31].

2.1.3. Filling the gap between Si electrodes with hex-SiNCs.
To fill the obtained Hex-SiNCs as thin films into the
gaps separating the Si electrodes, solutions of different
concentration of Hex-SiNCs in toluene were prepared and
tested, ranging from ~5 ng ml\(^{-1}\) to 20 mg ml\(^{-1}\). The samples
were first cleaned by sonication in acetone (10 min, VLSI
Selectipur, BASF), subsequent sonication in isopropanol
(VLSI Selectipur, BASF) and dry-blowing with N\(_2\),
followed by a short dip in diluted HF (2%, 30 s) to remove
the native oxide from the silicon electrodes’ surface, right
before the coating with Hex-SiNC solutions. Next, about
70 μl Hex-SiNC solution was immediately drop-casted onto
the sample covering the complete surface. We used a custom-
made device originally designed for nano-imprint lithography
to mechanically press the Hex-SiNC solution via a pressure-
transducing PDMS membrane into the gaps. The membrane
was fabricated by mixing base and curing agent (Sylgard 184
silicon elastomer kit, Dow Corning) in a weight ratio of 5:1:
evacuating the mixture in a desiccator to remove air bubbles
and curing it for 48 h at room temperature. In order to
mechanically press the Hex-SiNC solution into the gaps,
the volume between the PDMS membrane and the wetted sample
surface was evacuated by a standard membrane vacuum
pump, such that the PDMS membrane got into close contact
with the sample surface. Thus, the solvent of the drop-casted
Hex-SiNC solution on the sample was removed mainly by
pumping but also to a little amount by being soaked by the
PDMS membrane while mechanically pressing the Hex-
SiNCs as a thin film into the gap separating the electrodes. No
remaining solvent could be observed after 4 min of evacuation
and having carefully released the PDMS membrane from the sample surface. For every sample we
used a newly prepared, fresh piece of the same PDMS
membrane. After release, the samples were heated on a
hotplate to 100 °C for 60 s to evaporate remaining residues of the
solvent. To investigate the quality and filling height of the
Hex-SiNC thin film in the gap between electrodes, we used
reference samples based on the same SOI material and
fabricated a set of six very wide (w ≈ 7 mm, l = 200 nm)
gaps per reference sample by e-beam lithography and RIE
using the same fabrication and PDMS membrane coating
protocol as for the gap electrodes array samples described
before. All reference samples were coated with Hex-SiNC
solutions from the same batch that was used for the coating of the
gap electrode samples.

2.2. Characterization methods

2.2.1. Characterization of Hex-SiNCs. Upon surface
functionalization, presence of hexyl groups on the SiNC
surface was observed via FTIR (Fourier-Transform Infrared
spectroscopy (figure S12(a))). Presence of alkyl peaks between
2850 and 2955 cm\(^{-1}\) (CH\(_2\) and CH\(_3\) v-stretching) and at
~1462 and ~1378 cm\(^{-1}\) (CH δ-deformation) is a good
indication for a successful reaction [21]. The spectrum also
shows signals assigned for Si−H groups at ~2100, 906 and
660 cm\(^{-1}\), together with minor oxidation evidenced by the
Si−O bond at 1050 cm\(^{-1}\). The FTIR spectrum was collected
with a Bruker Vertex 70 FTIR using a Platinum ATR from
Bruker.

Transmission electron microscopy (TEM) revealed an
average SiNC size (diameter) of 3.1 ± 0.2 nm (figure S12(b)).
A histogram showing the size distribution is provided (figure
S12(c)). The mean and standard deviation was calculated by
measuring the size of 300 SiNCs. Bright field TEM images
were obtained using a JEOL-2012 electron microscope
equipped with LaB6 filament and operated at an acceleration
voltage of 200 kV.

2.2.2. Atomic force microscopy. AFM images were taken
with a Dimension V (Bruker/Veeco) AFM in tapping mode
equipped with a silicon tip, coated with a diamond-like-
carbon-coating (TAPI90DLC, BudgetSensors). Scan rate was
typically 1 Hz. Images were analyzed using the NanoScope
Analysis 1.5 software (Bruker).

2.2.3. X-ray photoelectron spectroscopy. X-ray photoelectron
spectroscopy (XPS) measurements were carried out in a home-
built setup (parts from SPECS Surface Nano Analysis) under
ultra-high vacuum (~6 × 10\(^{-9}\) mbar). The setup is equipped
with an XR 50 x-ray source and a Phoibos 100 hemispherical
electron analyzer. An aluminum anode was utilized, generating
x-ray photons of the energy of the Al K\(_\alpha\) edge (E = 1486.6 eV).
The x-ray source was operated at a voltage of 12.50 kV and an
emission current of 20.0 mA. Photoelectron spectra were
acquired at an energy resolution of 0.1 eV and a dwell time of
1 s and averaged over two to four scan repetitions. A pass energy
of 30 eV was used universally. XPS data were analyzed with
CasaXPS software (www.casaxps.com; charge referencing,
background subtraction and elemental analysis) and Origin
(intensity normalization and plotting). The spectra were charge-
referenced with respect to the C 1 s hydrocarbon peak at
284.8 eV and corrected for analyzer transmission and
photoelectron escape depth. For quantitative analysis and
normalization, relative sensitivity factors (Scofield cross-sections [32]) for each peak were retrieved from the CasaXPS library, accounting for the effective photoionization cross-section of the associated electronic transition. As reference samples for the XPS measurements, planar silicon substrates covered with ~100 nm titanium oxide (TiO2) were used. They were coated with Hex-SiNC thin films, analog to the gap separated Si electrode samples.

2.2.4. Electrical characterization. For electrical characterization, the finished sample devices were mounted in a vacuum probe station (TTPX, LakeShore), without delay. All electrode pairs were electrically characterized in darkness at room temperature, at a base pressure of $10^{-5}$–$10^{-6}$ mbar, by contacting the metal pads of each device with beryllium-copper probe needles. DC $I$–$V$ curves were measured at a scan rate of about 150 mV s$^{-1}$ using a source meter (Keithley 2635B) controlled by a PC (Matlab software).

3. Results and discussion

In advance to electrical characterization, we have studied in detail to what extent the Hex-SiNCs film thickness between silicon electrodes can be controlled using our pressure-transducing PDMS membrane technique. In fact, the level of gap filling can be efficiently adjusted by the concentration of SiNCs in solution.

As shown in the scanning electron microscopy (SEM) cross-sectional images of figure 2, the thin-film thickness ($h$) in the gap increases monotonically with the solution concentration of the Hex-SiNCs, which was varied from $c = 5, 10, 15$–20 mg ml$^{-1}$ (figures 2(b)–(e), respectively). In general, the film shape adopted a concave form inside the gap. Here, we determined the (minimum) film thicknesses $h$ from measuring in the middle of the cross section of the gap, as depicted in figure 1(f). Figure 2(f) summarizes the measured film thickness as function of Hex-SiNC solution concentration, starting from a thin film with $h \sim (15 \pm 3)$ nm up to an almost completely filled gap with $h = (92 \pm 8)$ nm. All resulting Hex-SiNC thin films filled the gap in a homogeneous manner, practically free from voids or cracks in the film or close to the interface to the electrodes: out of 80 examined cross-sections only one void was observed, and no cracks at all. This is an important requirement for stable and reproducible electrical measurements.

In order to obtain insight into the Hex-SiNC film composition, we measured the relative ratios of silicon to carbon in the Hex-SiNC thin films on planar surfaces, using XPS. For all films prepared from different solution concentrations, the measured Si-to-C ratios were in the range 87%–91%, hence showed very little variation (see, figure SI3 and table SI1). While a comparison of SiNC density for the different films cannot be derived from these results alone, still the composition of the organically functionalized SiNCs within each film neither did change as function of concentration nor was affected by the filling process, which is essential for comparing films of different thickness in electrical characterization.

Small residuals of PDMS could be identified by XPS, which can be assigned to the membrane-based preparation process. These are most likely located at the surface of the thin films and would therefore not affect the charge transport properties of the Hex-SiNCs networks. No distinct presence of SiO2 indicative of SiNC oxidation could be resolved by XPS (see supporting information).

We characterized the prepared Hex-SiNC films of different filling height $h$ electrically, by measuring the DC $I$–$V$ characteristics across the filled gaps. All gaps were of length $206 \pm 11$ nm, while their widths varied from 5 to 50 $\mu$m. Before measuring the coated samples, all devices were pre-characterized in their as-fabricated state, i.e. without any Hex-SiNC film filling. Only those fabricated devices with measured currents less than 1 pA at an applied voltage of 30 V (i.e. with insulating gap) were taken into further consideration for filling with Hex-SiNC films (see figure 3(a), gray curve, for such a reference measurement).

Figure 3(a) summarizes the $I$–$V$ characteristics of the investigated devices ($w = 20 \mu$m) filled with SiNC films, prepared from Hex-SiNCs solution concentrations 5, 10 and 20 mg ml$^{-1}$ that resulted in thin film thicknesses of about $h = 15, 23$ and 92 nm, respectively. After filling the gaps with these thin films, all devices showed a pronounced non-linear increase in current with increasing voltage, when compared to the empty, insulating device directly after fabrication. With increasing thin film thickness, a larger current
was measured over the entire voltage range. We note that the displayed curves are all averages from the very first bias scans from zero to 35 V. The reason for this choice of first curves was a pronounced hysteretic $I$–$V$ behavior, which was observed for all investigated samples. By selecting the same (first) traces, all samples with different filling could be compared. The hysteretic behavior led to notable differences for consecutive forward and backward scans, carried out between the minimal ($V = 0$ V) and maximal applied voltage. The inset of figure 3(a) shows the $I$–$V$ traces of three subsequent scans as an example. As additionally apparent from the inset, for subsequent bias scanning cycles the overall reached maximum currents successively decreased, until typically after some twenty cycles the currents had already dropped by some 80%–90% (see, figure S14). Yet, evaluating the first-scan data from 24 gap devices in total, we could determine the dependence of current as function of film thickness and channel width. As shown in figures 3(b) and (c), measured currents increased monotonically, roughly linearly as function of these two parameters, suggesting the well-defined, homogeneous filling of the gaps up to their edges. This is supported by an AFM image covering one full gap region, showing an overall homogeneous film with only minor surface undulation (see, figure S15).

We note that all measured currents correspond to a very low conductance regime, with values in the range of 10 pA or below, at 35 V. Corresponding specific conductivities are estimated to be in the range $10^{-10}$–$10^{-9}$ $\Omega^{-1}$ cm$^{-1}$, hence can be roughly compared with conductivities of materials such as intrinsic wide-band-gap semiconductors or insulators. Previously reported specific conductivities for alkyl-functionalized SiNCs, which were about three orders of magnitude larger, could be assigned to slight doping of these SiNCs [19].

Yet, our study revealing the monotonic, approximately linear dependence of current as a function of film thickness and gap width indicates that charge transport presumably takes place homogeneously through the Hex-SiNC layer. This charge transport medium consists of a randomly ordered network of (undoped) SiNCs which are separated by surface bound hexyl molecules. The hexyl molecule thickness sets the SiNC-to-SiNC distance to a minimum of roughly 1.6 nm, assuming dense packing (see supporting information). This organic, insulating spacer represents a barrier for charge carriers to be transferred from SiNC to SiNC. For the traveling of charges over the total distance of 200 nm, percolation paths across the randomly connected network of SiNCs are likely [33–36]. The transport along these paths may involve a hopping-type of charge transport [37], Fowler–Nordheim tunneling [38], Pool–Frenkel conduction [19] or space-charge-limited-current (SCLC) transport [39]. If localized charges trapped within the semiconductor SiNCs may build up gradually with time under applied bias and continuous injection from the source, the overall resulting space-charge layer in the SiNC material will increasingly block subsequent charge injection. As a consequence, the resulting current at a fixed bias decreases with time. In fact, such a behavior has been observed for networks of oxidized or hydrogen-terminated SiNCs and explained within this framework [40]. The observed hysteretic behavior and particularly the successive degradation of current upon cyclic voltage ramping qualitatively agree with such SCLC mechanism, and first quantitative parameters may be extracted from the data. Figure 4 displays the $I$–$V$ traces of figure 3(a) in a double-log plot. In this representation, two voltage ranges can be identified with disparate slopes, corresponding to a current–voltage dependence of the form $I = aV + bV^m$, with

![Figure 3](image-url)

Figure 3. (a) Current–voltage characteristics for devices with $w = 20 \mu m$, filled with films of Hex-SiNCs that were prepared from different solution concentrations. Data shows the first bias scan from zero to 35 V, averaged over two individual devices. The inset shows three consecutive $IV$ scans measured for the device prepared with a 4.6 mg ml$^{-1}$ Hex-SiNC solution. The black arrows indicate the scan direction for the example of the first scan. (b) Current at $V = 35$ V as function of Hex-SiNC thin film thickness for devices with widths 5, 10, 20 and 50 $\mu m$. The dashed lines are linear fits to the data points. (c) Current at $V = 35$ V as function of gap widths for different Hex-SiNC film thicknesses. The dashed lines are linear fits to the data points.
In summary, we have demonstrated that all-silicon electrode devices may serve as platform for the electrical characterization of thin films of functionalized, undoped SiNCs. A key factor to succeed in reliable measurements of these films in the high-resistance regime was a novel technique of filling the space between electrodes from solution, via a pressure-transducing PDMS membrane. This procedure led to homogeneous and dense thin films practically without any cracks or voids, and with precise control of the film thickness. The electrical functionality of our devices was demonstrated for thin films of hexyl functionalized SiNCs of various thicknesses, filled into the 200 nm trench separating the Si electrodes. Conductance was significantly enhanced compared to untreated devices. The obtained current–voltage (I–V) characteristics showed the anticipated scaling with channel width, ranging from 5 to 50 \( \mu m \), and with film thickness, ranging from 15 to 92 nm. A strongly hysteretic I–V dependence together with a successive decrease of current with time or with the number of I–V cycles can be assigned to SCLC-transport, with the functionalized SiNCs providing efficient charge trap centers. Future studies will focus on a microscopic understanding of this transport, including the influence of different SiNC surface-bound organic molecules, which can be varied over a wide range. Further, we plan to determine the actual contact resistance value (Si electrode to SiNC film) and its impact on charge injection.

We suggest our planar, all-silicon device architecture and functionalization methodology as platform for investigations of the transport properties of thin films of various hybrid nanomaterials, in particular in the high-resistance range.

Acknowledgments

We are grateful to Rui Pereira for helpful discussions. This work has been supported by the Deutsche Forschungsgemeinschaft DFG (IRTG 2022 ATUMS). A Angi is thankful for the funding from the Studienstiftung des deutschen Volkes.

ORCID IDs

Simon Pfaehler @ https://orcid.org/0000-0001-7156-7870
Arzu Angi @ https://orcid.org/0000-0002-6722-7408
Domenikos Chryssikos @ https://orcid.org/0000-0002-9239-8655
Anna Cattani-Scholz @ https://orcid.org/0000-0003-4974-8629
Bernhard Rieger @ https://orcid.org/0000-0002-0023-884X
Marc Tornow @ https://orcid.org/0000-0002-1860-2769

References

[1] Li X et al 2018 Bright colloidal quantum dot light-emitting diodes enabled by efficient chlorination Nat. Photon. 12 159–64
[2] Liu X et al 2018 Light-emitting diodes based on colloidal silicon quantum dots with octyl and phenylpropyl ligands ACS Appl. Mater. Interfaces 10 5959–66
[3] Kim J Y, Voznyy O, Zhitomirsky D and Sargent E H 2013 25th anniversary article: colloidal quantum dot materials and devices: a quarter-century of advances Adv. Mater. 25 4986–5010
[4] Liu J et al 2013 Assessing clinical prospects of silicon quantum dots: studies in mice and monkeys ACS Nano 7 7303–10
[5] Ledoux G, Gong J, Huisken F, Guillou O and Reynaud C 2002 Photoluminescence of size-separated silicon nanocrystals: confirmation of quantum confinement Appl. Phys. Lett. 80 4834–6
[6] Rinnert H, Jambois O and Vergnat M 2009 Photoluminescence properties of size-controlled silicon nanocrystals at low temperatures J. Appl. Phys. 106 023501
[7] Jurbergs D, Rogojina E, Mangolini L and Kortshagen U 2006 Silicon nanocrystals with ensemble quantum yields exceeding 60% Appl. Phys. Lett. 88 233116
[8] Zhao S et al 2018 Electroluminescent synaptic devices with logic functions Nano Energy 54 383–9
[9] Tan H et al 2018 Broadband optoelectronic synaptic devices based on silicon nanocrystals for neuromorphic computing Nano Energy 52 422–30
[10] Dasog M, Reyes G B D L, Titova L V, Hegmann F A and Veinot J G C 2014 Size versus surface: tuning the photoluminescence of freestanding silicon nanocrystals across the visible spectrum via surface groups ACS Nano 8 9636–48
[11] Angi A et al 2016 Photoluminescence through in-gap states in phenylacetylene functionalized silicon nanocrystals Nanoscale 8 7849–53
[12] Clark R J et al 2017 From hydrogen silsesquioxane to functionalized silicon nanocrystals Chem. Mater. 29 80–9
[13] Cheng X, Lowe S B, Reece P J and Gooding J J 2014 Colloidal silicon quantum dots: from preparation to the modification of self-assembled monolayers (SAMs) for bio-applications Chem. Soc. Rev. 43 2680–700
[14] Dohnalová K, Gregorkiewicz T and Kůšová K 2014 Silicon quantum dots: surface matters J. Phys.: Condens. Matter 26 173201
[15] Zhou T et al 2015 Bandgap tuning of silicon quantum dots by surface functionalization with conjugated organic groups Nano Lett. 15 3657–63
[16] Dasog M, Kehrle J, Rieger B and Veinot J G C 2016 Silicon nanocrystals and silicon-polymer hybrids: synthesis, surface engineering, and applications Angew. Chem., Int. Ed. 55 2322–39
[17] Zabet-Khosousi A and Dhirani A A 2008 Charge transport in nanoparticle assemblies Chem. Rev. 108 4072–124
[18] Le T H, Kim K J and Jeong H D 2017 Effect of thermal cross-linking of 4-Ethynylstyryl capping groups on electronic coupling between silicon quantum dot in silicon quantum dot solids J. Phys. Chem. C 121 15957–69
[19] Chen T, Skinner B, Xie W, Shklovskii B I and Kortshagen U R 2014 Carrier transport in films of alkyl-ligand-terminated silicon nanocrystals J. Phys. Chem. C 118 19580–8
[20] Ju Y C et al 2012 Resistance random access memory based on a thin film of CdS nanocrystals prepared via colloidal synthesis Small 8 2849–55
[21] Höhlein I M D, Angi A, Sinelnikov R, Veinot J G C and Rieger B 2015 Functionalization of hydride-terminated photoluminescent silicon nanocrystals with organolithium reagents Chemistry—Eur. J. 21 2755–8
[22] Lenz T et al 2016 Downsizing and charge transport in nanostructured ferroelectric memory diodes fabricated by solution micromolding Adv. Funct. Mater. 26 5111–9
[23] Ashwell G J et al 2010 Molecular bridging of silicon nanogaps ACS Nano 4 7401–6
[24] Corley D A, He T and Tour J M 2010 Two-terminal molecular memories from solution-deposited C60 films in vertical silicon nanogaps ACS Nano 4 1879–88
[25] Schukfeh M I et al 2016 Towards nanometer-spaced silicon contacts to proteins Nanotechnology 27 115302
[26] Pfaehler S et al 2016 A nanogap electrode platform for organic monolayer-film devices 16th Int. Conf. on Nanotechnology —IEEE NANO pp 842–4
[27] Govor L V, Bauer G H and Parisi J 2009 A simple method for filling nanogap electrodes with polymer Rev. Sci. Instrum. 80 033902
[28] Rydzek G et al 2015 Selective nanotrench filling by one-pot electroclick self-constructed nanoparticle films Small 11 4638–42
[29] Bank H M, Cifuentes M E and Theresa E M 1991 Process for the synthesis of soluble, condensed hydrosilicon resins containing low levels of silanol US Patent 5.010,159
[30] Angi A et al 2018 The influence of conjugated alkynyl(aryl) surface groups on the optical properties of silicon nanocrystals: photoluminescence through in-gap states Nanotechnology 29 355705
[31] Angi A et al 2018 The influence of surface functionalization methods on the performance of silicon nanocrystal LEDs Nanoscale 10 10337–42
[32] Scofield J H 1976 Hartree-Slater subshell photoionization cross-sections at 1254 and 1487 eV J. Electron. Spectrosc. Relat. Phenom. 8 129–37
[33] Aigner W, Wiesinger M, Wiggers H, Stutzmann M and Pereira R N 2016 Three-dimensional percolation and performance of nanocrystal field-effect transistors Phys. Rev. Appl. 5 2146
[34] Müller H, Wei G, Raguse B and Myers J 2003 Three-dimensional percolation effect on electrical conductivity in films of metal nanoparticles linked by organic molecules Phys. Rev. B 68 155407
[35] Rafiq M A et al 2006 Hopping conduction in size-controlled Si nanocrystals J. Appl. Phys. 100 014303
[36] Weis S et al 2011 Conduction mechanisms and environmental sensitivity of solution-processed silicon nanoparticle layers for thin-film transistors Small 7 2853–7
[37] Fu H, Reich K V and Shklovskii B I 2016 Hopping conductivity and insulator-metal transition in films of touching semiconductor nanocrystals Phys. Rev. B 93 125430
[38] Burr T, Seraphin A, Werwa E and Kolenbrander K 1997 Carrier transport in thin films of silicon nanoparticles Phys. Rev. B 56 4818–24
[39] Rafiq M A et al 2005 Charge injection and trapping in silicon nanocrystals Appl. Phys. Lett. 87 1–3
[40] Pereira R N et al 2011 Solution-processed networks of silicon nanocrystals: the role of internanocrystal medium on semiconducting behavior J. Phys. Chem. C 115 20120–7
[41] Rose A 1955 Space-charge-limited currents in solids Phys. Rev. 97 1538–44
[42] Lampert M A 1956 Simplified theory of space-charge-limited currents in an insulator with traps Phys. Rev. 103 1648–56
[43] Mott N F and Gurney R W 1950 Electronic Processes in Ionic Crystals 6th edn (Oxford: Clarendon)
[44] Furukawa S, Kagawa T and Matsumoto N 1982 Estimation of localized state distribution profiles in undoped and doped a-Si:H by measuring space-charge-limited current Solid State Commun. 44 927–30