Charge injection and trapping in silicon nanocrystals

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The temperature dependence of the conduction mechanism in thin films of ~8 nm diameter silicon nanocrystals is investigated using Al/Si nanocrystal/p-Si/Al diodes. A film thickness of 300 nm is used. From 300 to 200 K, space charge limited current, in the presence of an exponential distribution of trapping states, dominates the conduction mechanism. Using this model, a trap density \( N_t = 2.3 \times 10^{17} \text{ cm}^{-3} \) and a characteristic trap temperature \( T_t = 1670 \text{ K} \) can be extracted. The trap density is within an order of magnitude of the nanocrystal number density, suggesting that most nanocrystals trap single or a few carriers at most. © 2005 American Institute of Physics.

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In recent years, there has been great interest in silicon nanocrystals prepared by various growth techniques.\(^1\)-\(^4\) The nanometer-scale size of these crystals leads to novel electronic and optical properties associated with quantum confinement and single-electron charging effects. These properties have been exploited for the fabrication of single-electron transistors and memories,\(^1\)-\(^5\) electron emitters,\(^6\) and silicon light emitting devices.\(^7\) The possibility of precise control of the nanocrystal size and separation, e.g., by plasma decomposition of SiH\(_4\),\(^3\)-\(^7\) raises the possibility of large numbers of nanocrystal devices with well defined electrical and optical characteristics.

At present, there are only limited investigations of the macroscopic electronic conduction mechanism across Si nanocrystal films. While electronic transport through single nanocrystals shows strong single-electron charging effects at low temperatures,\(^8\) it is not clear if this occurs in large numbers of nanocrystals. At high bias, it is possible to observe electron emission from thin films of nanocrystals.\(^5\) In investigations of the electrical and electroluminescence characteristics of Si nanocrystals prepared by pulsed laser ablation, a space charge limited current (SCLC) and tunneling conduction mechanism has been suggested.\(^10\) In contrast, there are detailed investigations of carrier transport in porous Si films (which may contain silicon nanocrystals), and in other systems such as CdSe nanocrystals, where SCLC electron transport has been demonstrated explicitly.\(^11\)-\(^14\)

This letter investigates the macroscopic electronic conduction mechanism across 300-nm-thick Si nanocrystal films with ~8 nm diameter nanocrystals. We measure the temperature dependence of the \( I-V \) characteristics of Al/Si nanocrystal/p-Si/Al diodes from 300 to 40 K. From 300 to 200 K, the conduction mechanism is dominated by SCLC transport, in the presence of an exponential distribution of trapping states. Using this model, we extract a trap density \( N_t = 2.3 \times 10^{17} \text{ cm}^{-3} \) and a characteristic trap temperature \( T_t = 1670 \text{ K} \). The trap density was within an order of magnitude of the nanocrystal number density, suggesting that most nanocrystals trap single or a few carriers at most.

Figure 1(a) shows a schematic diagram of our device. The device uses a ~300 nm thick Si nanocrystal film, deposited by plasma decomposition of SiH\(_4\) (Ref. 1) on a p-Si substrate (resistivity: 10 \( \Omega \) cm). The nanocrystals are 8 nm±1 nm in diameter and undoped, with a ~1.5-nm-thick surface SiO\(_2\) layer, at least for nanocrystals near the film surface. Figure 1(b) shows a scanning electron micrograph of...
The increase in 200 K, the curves do not converge towards a single point, but with increasing  from 300 to 200 K, and increasing voltage threshold, from 1.2 to 4 V. The increase in  leads to convergence of the I-V characteristics from 300 to 200 K, such that the different curves can be extrapolated to meet at a single point (see Fig. 3). Below 200 K, the curves do not converge towards a single point, and instead tend to a constant slope. For low voltages, e.g., below ~1.2 V at 300 K, the current can be shown to increase exponentially. In order to confirm that the behavior of Fig. 2(a) is due to the Si nanocrystal layer and not due to the p-Si substrate, we have also measured the temperature dependence of the I-V characteristics between two Al substrate contacts, from 300 to 40 K. These curves show an exponential I-V dependence and do not show the dependence of Fig. 2(a). The current in these curves also remains larger than in Fig. 2(a), implying that in our Al/Si nanocrystal/p-Si/Al structure, there is a lower resistance for the p-Si substrate/Al substrate-contact part than for the top Al contact/Si nanocrystal part. Therefore, the dependence of Fig. 2(a) can be associated with the top Al contact/nanocrystal film.

The characteristics from 300 to 200 K can be explained using a SCLC model with an exponential density of traps, and free carriers are injected from the substrate into transport states in the film [Fig. 2(b)]. An exponential distribution of traps above these states reduces the number of free carriers. With increasing voltage, the Fermi level fall through the distribution, filling the traps and causing a rapid increase in free carriers. Assuming a constant mobility, a free carrier concentration much less than the trapped carrier concentration, an exponential trap distribution, and considering only majority carriers (in our case, holes from the substrate), the current density is

\[
J = q^2l^{-1}\mu_pN_f\left(\frac{2l + 1}{l + 1}\right)^{\frac{1}{l + 1}}\left(\frac{1 - \varepsilon_0\varepsilon_t}{l + 1 N_f}\right)^{\frac{l + 1}{l + 1}} \left(\frac{l}{d}\right)^{2l + 1}.
\]

Here, \(N_f\) is the trap density, \(\varepsilon_0\) is the permittivity of free space, \(\varepsilon_t\) the dielectric constant, \(\mu_p\) the hole mobility, \(N_g\) is the density of transport states, \(d\) is the sample thickness, and \(l/T_f/T_i\), where \(T_f\) is the measurement temperature and \(T_i\) the characteristic temperature. \(T_i\) is related to the characteristic energy of the trap distribution, \(E_t = k_B T_i\), where \(k_B\) is the Boltzmann constant. Equation (1) predicts a \(J-V^m\) dependence, where \(m = l + 1\). Thus, the slope of a log-log plot of \(J-V\) directly determines the characteristic temperature and energy.

Figure 3 shows SCLC power law fits to the data of Fig. 2(a) from 280 to 200 K, where the data converges to \(V_c = 17\) V and the slopes give the exponent \(m\). The inset shows that \(m\) increases linearly as a function of inverse temperature, as predicted by SCLC theory. Here, \(T_f = 1670\) K, and \(E_t = 0.14\) eV. Below ~200 K, the curves tend to a constant \(m\) and the SCLC model does not fit. This is because the thermal
energy is not sufficient to ionize carriers between the traps and the transport states. Carrier transport at these temperatures can occur by hopping conduction.\textsuperscript{11,16} In our data at low temperature, the conductance can be shown to follow a $T^{-1.2}$ law, corresponding to variable range hopping with Coulomb interactions.\textsuperscript{17}

Equation (1) can be approximated in an Arrhenius form\textsuperscript{18}

$$J = \frac{1}{2} \left( \frac{\mu_p N_e q V}{d} \right) \exp \left[ - \frac{E_t}{kT} \left( \ln \left( \frac{q N_e d^2}{2 e \varepsilon_0 V} \right) \right) \right],$$

where the activation energy is

$$E_a = \frac{E_t}{k} \left( \ln \left( \frac{q N_e d^2}{2 e \varepsilon_0 V} \right) \right).$$

This relates the slope of the ln($J$) vs $1/T$ curves at constant voltage to the total trap density. An examination of Eq. (2) shows that the current is temperature independent at a “crossover voltage” $V_c$, where $E_a = 0$ and

$$V_c = \frac{q N_e d^2}{2 e \varepsilon_0}.$$

If the curves of Fig. 2(a) from 300 to 200 K are extrapolated, then it is possible to obtain the crossover voltage $V_c$. Figure 3 shows this data, with $I \propto V^{n_1}$ fits to the data (solid lines) extrapolated to find $V_c$. Here, $V_c = 17$ V, which gives $N_e = 2.3 \times 10^{17}$ cm$^{-3}$. In addition, if we plot our data in an Arrhenius plot [ln($I$) vs $1/T$], we can directly measure $E_a = 200$ meV at a bias of 4 V. This gives $N_e = 2.4 \times 10^{17}$ cm$^{-3}$ [Eq. (3)], which is close to $N_e$ determined from the crossover voltage [Eq. (4)].

Our value of $N_e$ is very similar to the nanocrystal number density, $N_{nc} \sim 1.2 \times 10^{18}$ cm$^{-3}$. This suggests that only a few carriers are trapped per nanocrystal. With SCLC, holes are injected from the substrate into the nanocrystal film. A potential well may exist on each nanocrystal, between potential barriers at the nanocrystal surface. Single-electron or quantum confinement effects could then lead to a discrete density of states in the well.\textsuperscript{11,18} If the higher charge number states, closer to the top of the potential barrier, were delocalized then only a few localized (trapping) states would exist on a nanocrystal. This would limit the number of carriers trapped in the well and explain our similarity between $N_e$ and $N_{nc}$.

Alternatively, the trapping states may be formed by only a small number of defect states per nanocrystal. The values of $T_c = 1670$ K (corresponding to $E_t = 0.14$ eV) and $N_e = 2.3 \times 10^{17}$ cm$^{-3}$ can be compared to amorphous Si and to other nanocrystal systems. $T_c$ does not lie in the range observed for bulk amorphous Si ($\sim 300$–$1300$ K) or for large ($\sim 150$ nm) amorphous Si nanoparticles, and $N_e$ is two orders of magnitude smaller than in amorphous Si.\textsuperscript{19,20} Our values of $T_c$ and $N_e$ are more comparable to values observed in CdSe nanocrystals, similar in size to our Si nanocrystals, In CdSe, $T_c \sim 1750$ K, $E_t = 0.15$ eV, and $N_e \sim 10^{16}$–$10^{17}$ cm$^{-3}$ \textsuperscript{13,14} We speculate that our traps may be associated with nanocrystal size. Our ratio $N_{nc}/N_e$ $\approx 5$ is lower than in CdSe nanocrystals, where a ratio of 100 was observed for deep level traps.\textsuperscript{14} This suggests more uniform charging in our Si nanocrystals films.

In conclusion, we investigated the conduction mechanism in 300-nm-thick Si nanocrystal films, with $\sim 8$ nm nanocrystals. From 300 to 200 K, we observed SCLC hole transport with an exponential distribution of trapping states, where the trap density was $2.3 \times 10^{17}$ cm$^{-3}$ and the characteristic trap temperature was 1670 K. The trap density was within an order of magnitude of the nanocrystal number density, suggesting that most nanocrystals trap single or a few carriers at most.

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