Field-dependant hopping conduction in silicon nanocrystal films

M. A. Rafiq,^{1,a),b)} Z. A. K. Durrani,^{2,a)} H. Mizuta,^{3,a)} M. M. Hassan,⁴ and S. Oda^{1,a)}

¹Quantum Nanoelectronics Research Centre, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

²Department of Electrical and Electronic Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom

³Nanoscale Systems Integration Group, School of Electronics and Computer Science, University of Southampton, Southampton SO17 1BJ, United Kingdom

⁴Pakistan Institute of Engineering and Applied Sciences, Islamabad 45650, Pakistan

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We investigate the electric field dependence of hopping conduction in 300 nm thick films of ~ 8 nm diameter silicon nanocrystals. The hopping conductivity σ follows a $\ln(\sigma) \propto 1/T^{1/2}$ dependence with temperature T , explained by a percolation hopping conduction model. At high fields $F > \sim 1 \times 10^5$ V/cm, the hopping conductivity follows a $\ln(\sigma) \propto F^{1/2}$ dependence. This dependence is investigated using the concept of “effective temperature,” introduced originally by Shklovskii for hopping conduction in disordered materials. © 2008 American Institute of Physics.

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I. INTRODUCTION

In recent years, there has been great interest in systems of disordered material formed by semiconductor nanocrystals embedded in insulating matrices.^{1–6} Semiconductor nanocrystals, naturally formed by material synthesis, provide a means for the “bottom up” fabrication of nanoscale devices of increased functionality. In particular, silicon nanocrystals (SiNCs) are of great interest, as silicon is the material of choice for device fabrication. SiNCs have now been used to fabricate a variety of nanoscale devices, including single-electron transistors,⁷ nonvolatile memories,⁸ electron emitters using SiNCs films (60 nm–1.5 μm),⁹ and optoelectronic devices.¹

Conduction in nanocrystal films at low temperatures occurs by a hopping transport mechanism,^{4,10} a process that can depend upon both temperature and applied electric field. This is due to the fact that in a random hopping system, carrier jumps to localized states at higher energies can be facilitated either by phonon interaction or by a reduction in the hopping energy barrier by an external electric field. There are, however, only few studies of the field dependence of hopping conduction in semiconductor nanocrystals.¹⁰ In particular, the field dependence of hopping conduction in films consisting of semiconductor nanocrystals dispersed in insulating matrices remains to be investigated in detail.

In our previous work, we investigated the conduction mechanism in thin films of SiNCs surrounded by SiO_2 shells, prepared by plasma decomposition of silane.¹ At electric field $F > \sim 1 \times 10^5$ V/cm and temperatures T from 40 to 200 K, the conductivity σ followed a $\ln(\sigma)$ versus $1/T^{1/2}$ dependence,¹¹ explained by the percolation hopping conduction model developed by Šimánek.¹² At temperatures greater

than 200 K, space charge limited current has been observed.¹³ Recently, we reported the effect of SiNC diameter change on hopping conduction across SiNC films.¹⁴ However, the electric field dependence of hopping conduction across these films remained to be investigated.

In this paper, we investigate the electric field dependence of hopping conduction in SiNC films. We characterize our films using Al/*p*-Si/SiNC film/Al diodes, where the SiNC film thickness is ~ 300 nm. Each SiNC in the film is ~ 8 nm in diameter, and is encapsulated by a ~ 1.5 nm SiO_2 shell. From 200 to 40 K, a $\ln(\sigma)$ versus $1/T^{1/2}$ dependence is observed, similar to our previous work. At electric fields $F > \sim 1 \times 10^5$ V/cm, the hopping conduction follows a $\ln(\sigma)$ versus $F^{1/2}$ dependence. This behavior is investigated using the concept of “effective temperature” developed by Shklovskii.¹⁵

II. EXPERIMENT

The Al/*p*-Si/SiNC film/Al diodes were prepared by depositing SiNC films on *p*-Si substrates, similar to our previous devices.^{11,13} SiNC deposition was at room temperature, using the plasma decomposition of SiH_4 .¹ Figure 1(a) shows a scanning electron micrograph of the SiNC film. The SiNC film thickness is ~ 300 nm, and the SiNCs are 8 ± 1 nm in diameter.¹ Each SiNC is covered by a ~ 1.5 nm thick SiO_2 shell. Figure 1(b) shows a transmission electron micrograph of a ~ 10 nm diameter SiNC. The Al/*p*-Si/SiNC film/Al diodes were fabricated using mesa structures in the SiNC film, defined by electron beam lithography and reactive ion etching, similar to our previous work.^{11,13} The diode area, determined by the top Al contact area, varied from 35×35 to $200 \times 200 \mu\text{m}^2$.

III. RESULTS AND DISCUSSIONS

Our electrical characteristics were measured using a cryogenic temperature probe station (BCT-43MDC, from Nagase & Co. Ltd., Japan), and an Agilent 4156A parameter

^{a)}Also at SORST JST (Japan Science and Technology).

^{b)}Also at National Centre for Nanotechnology, Pakistan Institute of Engineering and Applied Sciences, Islamabad, Pakistan. Electronic mail: aftab@cantab.net.

FIG. 1. (a) Scanning electron micrograph of the SiNC film. (b) TEM image of a 10 nm diameter SiNC. (c) IV characteristics of device C from 40 to 200 K with a temperature step of 20 K.

analyzer. A positive voltage is applied to the *p*-Si substrate [inset to Fig. 1(c)] and conduction occurs by hole-injection from the substrate. We measure σ in four devices, devices A, B, C, and D, with areas of 35×35 , 65×65 , 100×100 , and $175 \times 175 \mu\text{m}^2$, respectively. Our characteristics were measured from 200 to 40 K, with a temperature step of 20 K. The current-voltage (*IV*) curves [Fig. 1(c)] were rectifying and asymmetric. We observe a $\ln(\sigma)$ versus $1/T^{1/2}$ temperature dependence in all four devices, similar to the characteristics reported in our earlier work.¹¹ Figure 2(a) shows the data for device C, for three different values of electric field. Here, the electric field F is defined as ratio of the applied voltage V to our SiNC film thickness (300 nm).

FIG. 2. (a) $\ln(\sigma)$ vs $1/T^{1/2}$ plot for device C at fields (1) $F=1.3 \times 10^5$ V/cm, (2) 2×10^5 V/cm, and (3) 2.7×10^5 V/cm. (b) Variation in T_0 as a function of field F .

The temperature dependence may be explained by the Šimánek model of percolation hopping conduction,¹⁵ where thermally activated carrier tunneling between adjacent nanocrystals, i.e., nearest neighbor hopping, is considered. The nanocrystal size d and separation s are regarded as random, uncorrelated variables. The hopping activation energy E_a is taken to be the energy difference between the first electron levels E_1 on neighboring nanocrystals. Here, $E_1 = E_c + E_d$, where E_c is the single-electron charging energy and E_d is the quantum confinement energy. According to this mechanism, the conductivity is given by

$$\sigma \propto \exp \left[- \left(\frac{T_0}{T} \right)^{1/2} \right]. \quad (1)$$

At low bias, the characteristic temperature T_0 is a constant of the material and is given by

$$T_0 = \frac{2P_c s_{\max} E_{a,\max}}{k_B a}. \quad (2)$$

Here, k_B is the Boltzmann constant, P_c is the percolation threshold, $s_{\max}$ is the maximum particle separation, a is the carrier wave function decay length in the insulating matrix, and $E_{a,\max}$ is the maximum activation energy for hopping. P_c is unknown for SiNCs films. However according to Ziman,¹⁶ in both ordered and disordered lattices, P_c follows the empirical formula $P_c \approx 1.5/Z$, where Z is the coordination number. Here we use an average value of $P_c = 0.25$ (corresponding to a simple cubic lattice) as an approximation.

In Fig. 2(a) as F increases, T_0 reduces. Figure 2(b) shows the reduction in T_0 as a function of electric field F . Therefore, increasing F reduces the effect of temperature on σ , i.e., at higher F there is a smaller change in σ over the same range of temperature. Equation (2) suggests that T_0 would reduce if $E_{a,\max}$ reduces. This is possible as increasing F reduces the hopping energy barriers.¹⁰ It is difficult to measure T_0 at fields below $F \sim 1 \times 10^5$ V/cm due to reduction in current levels and an increase in the noise. The reduction in current levels is caused by the applied voltage dropping below the threshold voltage [Fig. 1(c)].

Equation (2) may be used to determine the theoretical value of $T_0 = 1 \times 10^4$ K, described in detail in our previous work.¹¹ This value is valid for low bias, where $E_{a,\max}$ is not perturbed by F . We may compare the theoretical value of T_0 to our experimental values at low bias, extracted from the slope of the $\ln(\sigma)$ versus $1/T^{1/2}$ plot. At $F = 1.33 \times 10^5$ V/cm, T_0 for devices A, B, C, and D is 1.24×10^4 , 0.81×10^4 , 0.77×10^4 , and 0.83×10^4 K, respectively. The average value of T_0 is 0.91×10^4 K. The areas of devices A, B, C, and D is 35×35 , 65×65 , 100×100 , and $175 \times 175 \mu\text{m}^2$, respectively. The average value of T_0 varies $\pm 35\%$ with respect to mean value of T_0 . The observed variation in the value of T_0 may be associated with nonuniformity within the SiNC film. The average value of T_0 is in good agreement with our theoretical value of 1.0×10^4 K.

We now investigate the effect of F on σ . Figure 3(a) shows a $\ln(\sigma)$ versus $F^{1/2}$ plot for device C at fields $F > \sim 1 \times 10^5$ V/cm, as the temperature varies from 40 to 160 K in 20 K steps. It is seen that the conductivity follows a $\ln(\sigma)$

FIG. 3. (a) $\ln(\sigma)$ vs $F^{1/2}$ plot for device C. T is varied from 40 to 140 K, in 20 K steps. (b) F_0 vs T plot, where F_0 is the slope of the $\ln(\sigma)$ vs $F^{1/2}$ characteristics given in (a). The solid line is aid to the eyes.

versus $F^{1/2}$ dependence. Furthermore, the slope of these characteristics reduces with increasing temperature, consistent with the behavior of Fig. 2(a). We observe similar characteristics in all four devices. Figures 2(a) and 3(a) illustrate that the conductivity in our films depends on both electric field and temperature. The electric field dependence of the conductivity in our devices can be expressed as

$$\sigma \propto \exp \left[+ \left(\frac{F}{F_0} \right)^{1/2} \right]. \quad (3)$$

In our data, F_0 increases as the temperature increases from 40 to ~ 140 K.

Hohl *et al.*¹⁷ explained an $\ln(\sigma)$ versus $F^{1/2}$ dependence in films of cobalt nanoclusters surrounded by dielectric shells using the concept of effective temperature in hopping transport, introduced by Shklovskii.^{15,17} The morphology of our SiNC films is somewhat similar. The effective temperature model considers the influence of T and F on the hopping conductivity, using a single quantity $T_{\text{eff}}(T, F)$, the effective temperature. Following the approach of Hohl *et al.*, T_{eff} may be generally expressed as

$$T_{\text{eff}} = [T^\beta + (AF)^\beta]^{1/\beta}. \quad (4)$$

Here the factor AF has units of temperature and β is a constant. In the expression given by Hohl *et al.*, $A = \gamma e \alpha / k_B$, where α is the hopping length and γ is a further constant. A is therefore proportional to the hopping length. Equation (4) also uses the externally applied field F . Typically, T_{eff} is defined using F_h , the field between two hopping sites, and $e \alpha F_h$ gives the energy gained by a hopping electron from F_h .^{17,18} In Eq. (4), we assume that $F \propto F_h$, i.e., $F = c F_h$ and that the proportionality constant c is included in A .

The dependence described by Eq. (3) can be obtained by substituting Eq. (4) for T in Eq. (1), with $\beta = 1/2$ and using $AF \ll T$.¹⁷ This gives the following expression:

$$\sigma \propto \exp \left[- \left(\frac{T_0}{T} \right)^{1/2} + \left(\frac{F}{F_0} \right)^{1/2} \right]. \quad (5)$$

Here, $F_0 = T^2 / T_0 A$. Equation (5) predicts $\ln(\sigma) \propto F^{1/2}$ at constant T , giving the field dependence of our data [Fig. 3(a)].

We investigate the effective temperature model further by investigating the temperature dependence of F_0 . Figure 3(b) shows F_0 [extracted from the data of Fig. 3(a)] as a function of T , from 40 to 140 K. Figure 3(b) shows that $F_0 \propto T$. However, in Eq. (5), $F_0 = T^2 / T_0 A$ and if A is constant, then $F_0 \propto T^2$. Our data do not fit this dependence. However, if A varies linearly with T , then this predicts our observed $F_0 \propto T$. In the effective temperature model, A is proportional to the hopping length α . We therefore suggest that in our SiNC films, $\alpha \propto T$. This is possible as increased temperature reduces the effect of the barrier heights between the SiNCs and therefore, a longer localization length becomes possible.¹⁰

We comment briefly on the possibility of the Poole–Frenkel effect in our films. This also predicts a $\ln(\sigma)$ versus $F^{1/2}$ dependence, caused by the field-enhanced thermal excitation of trapped carriers.¹⁹ Our SiNC films are however strongly inhomogeneous, and in such a system, the Poole–Frenkel effect may not be a suitable description.¹⁷ Furthermore, the Poole–Frenkel model leads to an unrealistic estimation of the dielectric constant of our film by two orders of magnitude.

IV. CONCLUSIONS

In conclusion we investigated the electric field dependence of hopping conduction in SiNCs films, from 40 to 200 K. We observe a $\ln(\sigma) \propto (F/F_0)^{1/2}$ dependence at fields $> 1 \times 10^5$ V/cm, where F_0 varies linearly with temperature. This dependence is investigated using the effective temperature model for hopping transport in disordered materials.

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