Silicon nanoclusters (NCs) sensitize the luminescent 4f-shell transitions in the rare earth ions,\textsuperscript{1–3} with Er\textsuperscript{3+} being most widely studied because of its fluorescence near 1.53 \textmu m.\textsuperscript{4} By employing nanocrystals as sensitizers, the rare earths can be excited nonresonantly, and the absorption cross-sections—normally in the order of 10\textsuperscript{-20} \text{cm}\textsuperscript{2}—become effectively similar to those of the NCs (\sim 10\textsuperscript{-16} \text{cm}\textsuperscript{2}).\textsuperscript{3} This has led to several technical advances, including the initial effects similar to those of the NCs whose characteristic length is approximately 0.5 nm for crystalline ones.\textsuperscript{14} Here, the relationships will be derived for both energy transfer processes when the D and A species are contained in separate thick planes.

The transfer rate between two point dipoles is \( w_{Tr} = w_{PL}(R_0/r)^6 \), where \( w_{PL} \) is the donor photoluminescence (PL) rate and \( R_0 \) is the distance at which \( w_{Tr} = w_{PL} \). Treating the emitter as a single point and integrating the transfer rate over a plane of radius \( r \) of acceptor molecules (of number per unit area \( a \)) separated by a perpendicular distance \( x \) from the donor yields

\[
w_{Tr} = w_{PL} a \sigma \int_0^\infty \frac{2 \pi v}{(x^2 + y^2)^3} dy = \frac{\pi w_{PL} \sigma \gamma R_0^6}{2x^4},
\]

where \( \gamma \) is the homogeneously distributed orientation factor.\textsuperscript{16–18} When the transfer rate is averaged over a thin donor plane, one obtains the trivial result identical to Eq. (1). In order to obtain the average transfer rate between a donor and an acceptor plane of thicknesses \( t_D \) and \( t_A \), respectively, separated by a spacer of thickness \( x \), we have

\[
w_{Tr}(x) = \frac{1}{t_A} \int_x^{x+t_D} \left[ \frac{1}{t_D} \int_{x+y}^{x+y+t_A} \frac{\pi w_{PL} \sigma \gamma R_0^6}{2(x'^2+y'^2)} dx' \right] dy
\]

\[
= \frac{\pi w_{PL} \sigma \gamma R_0^6}{12 t_D t_A} M(x),
\]

where

\[
M(x) = 1/(x+x_0)^2 - 1/(x+x_0+t_d)^2 - 1/(x+x_0+t_d)^2 - 1/(x+t_d)^2.
\]

Here, \( x_0 \) is the minimum D-A separation distance taken as one bond length (\( x_0 \approx 0.3 \text{ nm} \)) from the D plane. Next, normalizing the D intensity \( I_D(x) = w_D^D/(w_{PL} + w_{Tr}) \) to its intensity at \( x = \infty \),

\[
I_D^D_{norm} = \frac{I_D(x)}{I_D(\infty)} = \frac{1}{1 + \frac{\pi \gamma \sigma R_0^6}{12 t_D t_A} M(x)}.
\]

Similarly, the acceptor intensity can be normalized to that at \( x = x_0 \),

\[
I_A^D_{norm} = \left[ \frac{12 t_D t_A}{\pi \gamma \sigma R_0^6 M(x_0)} + 1 \right]^{-1} \left[ \frac{12 t_A t_D}{\pi \gamma R_0^6 M(x)} + 1 \right].
\]

These equations are shown in Fig. 1(a) for different values of \( R_0 \). The two following features are apparent: (i) the interac-

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\textsuperscript{4}Electronic mail: ameldrum@ualberta.ca.
The normalized donor intensity has a form similar to Eq. \( \frac{I_{D}}{I_{A0}} \) for the Förster transfer. The numbers beside the curves represent the associated thickness across the wafer. The black line shows the acceptor intensity for point-to-point Förster transfer. The black line shows the acceptor intensity for point-to-point Förster transfer.

The plane-to-plane transfer rate for the Dexter exchange interaction can be solved by integrating the acceptor plane. The plane-to-plane transfer rate for the Dexter exchange interaction can be solved by integrating the acceptor plane. The plane-to-plane transfer rate for the Dexter exchange interaction can be solved by integrating the acceptor plane.

\[
\frac{I_{D}}{I_{A0}} = \frac{2 \pi \kappa_{D} e^{-b s}}{b^4 t_{d} t_{b} d} \left[ r(b s) + s \right].
\]

Here, \( r = (1 - e^{-b s})(1 - e^{-b d}), \) \( s = 3(1 - e^{-b s})(1 - e^{-b d}) - b t_{d} e^{-b s}(1 - e^{-b d}) - b t_{b} e^{-b d}(1 - e^{-b s}), \) and \( w_0 \) is a prefactor. The normalized donor intensity has a form similar to Eq. (3), where \( I_{norm}^{D} = \frac{I_{D}}{I_{A0}} \), with \( I_{norm}^{D} \) given by Eq. (5), and the normalized acceptor intensity is \( I_{norm}^{A} = \frac{I_{A}}{I_{A0}} \). These equations cannot be further simplified because of the parameter \( w_0 \).

Figure 1(b) shows that for a given \( 1/b \) the effects occur over shorter distances if the interacting species are in thick planes.

In order to compare with the theory, a multilayer thin film was deposited on a quartz substrate. The layers consisted of, in order from the bottom: 180 nm SiO\(_2\), 5 nm SiO (NC layer), 0–40 nm SiO\(_2\) (“spacer” layer graded in thickness across the wafer), 140 nm SiO\(_2\):Er (1.15 × 10\(^{19}\) Er\(^{3+}\)/cm\(^3\)), and a 130 nm SiO\(_2\) cap (Fig. 2). The sample was annealed at 1000 °C in flowing N\(_2\):H\(_2\) gas to precipitate passivated Si NCs in the SiO\(_2\) layer. The layer thicknesses and compositions were confirmed by Rutherford backscattering spectrometry (RBS) using the QUARK data analysis program, and TEM was performed on a JEOL 2200 FESEM. PL spectroscopy used standard methods described elsewhere.

The laser wavelength was 476 nm, which is not resonant with any Er\(^{3+}\) transition.

Figure 3 shows the donor (Si-NCs) and acceptor (Er\(^{3+}\)) fluorescence as a function of buffer layer thickness from 0 to 20 nm. The inset shows the Si NC PL intensity (which peaked at ~770 nm) as a function of buffer thickness, with a fit from Eq. (3).
emission as a function of the spacer thickness. The structure in the spectrum is due to crystal-field-splitting in silica, in which the F1 and F7 Er\textsuperscript{3+} subpeaks are characteristically the strongest.\textsuperscript{21} The intensity follows a trend that can be fit with Eqs. (3) and (4) ($R^2 = 0.9$) with a single fitting parameter $R_0$. Estimating $\sigma = 0.24$ nm$^{-2}$ from the RBS measurements and $\gamma = \pi/3$,\textsuperscript{16} yielded a mean effective $R_0$ value of 7.0 nm in the fitting of the acceptor PL, or 5.8 nm for the donor PL. The NC PL data trended appropriately but was more scattered than the data for Er\textsuperscript{3+}. Similar or larger $R_0$ values have been reported for Eu\textsuperscript{3+} and Tb\textsuperscript{3+} with organic molecular sensitizers.\textsuperscript{22} By fitting the same data for the $1/r^6$ point-to-point energy transfer, $R_0$ becomes 2.8 nm—in close accord with previous estimates; however, with a much steeper dependence on separation distance than observed in the data [Fig. 3(b)]. Effectively, the planar geometry “smoothes” the $r^{-6}$ dependence and makes it look exponential. In comparison, a characteristic distance of 5.0 nm was found by fitting the point-to-point exchange function to the acceptor PL—also in agreement with previous work\textsuperscript{21}—but with a nonphysically large transfer distance. Even larger exchange distances would be required for plane-to-plane transfer, as shown in Fig. 1(b). Finally, the lifetime of the NC emission followed the stretched exponential function $\exp[-(t/\tau)^{\beta}]$, with $\beta$ between 0.6 and 0.7 and lifetimes ranging from 40 $\mu$s for a 1 nm spacer thickness up to 55 $\mu$s in without the Er-doped layer. This difference is smaller than expected for $R_0$ values estimated here but the analysis does not include the stretched exponential factors or NC-NC interactions.\textsuperscript{23} Nevertheless, the shorter lifetimes found for a thinner spacer is consistent with the transfer effect. In order to calculate a single transfer time from a random distribution of NCs and Er\textsuperscript{3+} (as in most samples), one can integrate the transfer rate for acceptors distributed uniformly around a point dipole as $\frac{w_{dip} R_0^6 \rho_0}{4 \pi \alpha^2} dr$, indicating that the effective transfer time is sensitive to the chosen minimum NC-Er separation. With the distance $r_0 = 0.3$ nm and $R_0 = 7$ nm, we have $w_{dip}$ of $\sim 10^9$ s$^{-1}$. This rate is consistent with the “fast” transfer process reported previously\textsuperscript{24,25} but not with the much slower processes also reported.\textsuperscript{26,27} However, the calculated rate decreases quickly ($r_0^{-6}$) for minimum distances greater than 0.3 nm.

Although Eqs. (3)–(5) are analytical solutions, there are experimental sources of error. First, we can only obtain an effective $R_0$ that is averaged over the entire NC size distribution and the resulting phonon-assisted transfer rates. Additional effects that can impact the estimated transfer distances include possible erbium diffusion into the spacer during annealing, NC-NC energy transfer, and the size of the NCs which is significant compared to the transfer distances. Despite these issues, however, Eqs. (3)–(5) are general for any planar geometry of atoms or molecules interacting via the Förster or Dexter mechanisms. Essentially, both mechanisms can fit the data for Si NCs and Er\textsuperscript{3+}, but with nonphysically long-range interactions for the Dexter case. For Si NCs and Er\textsuperscript{3+}, an $R_0$ in the range of 6–7 nm is larger than a previously estimated interaction distance for this system,\textsuperscript{14} but is comparable to those for rare earths sensitized by organic molecules,\textsuperscript{22} and is within the theoretical range for Si NC-NC transfer as well.\textsuperscript{26} In conclusion, the long interaction distance for Si NCs and Er\textsuperscript{3+} is consistent with a strong sensitizing effect that could be important in applications ranging from waveguide amplifiers to fluorescence imaging with silicon nanocrystals.

The authors are funded by NSERC and iCORE. Thanks to M. Malac and P. Li for TEM data [NINT Electron Microscopy Facility (NRC)] and to Dr. P. Bianucci and an anonymous referee for critical reviews.

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