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ABSTRACT
We report on the quantum confined Stark effect coupled with a permanent built-in electric dipole moment in size-controlled Si nanocrystals (SiNCs) investigated under steady state conditions by photoluminescence spectroscopy. The study was conducted on samples with SiNC layer thicknesses between 2 nm and 5 nm. The emission spectra of the samples subjected to electric field magnitudes of up to $5 \times 10^8$ V/m were analyzed in terms of the dependency of the spectral shift on field magnitude and SiNC size. A clear trend of red shift along with increasing dipole separation was observed with increasing SiNC size. Experimental results show a high degree of accuracy to the model based on the time independent perturbation theory approximation for a biased quantum well. We propose a potential application for size-controlled SiNCs in photon detection in the near infrared band based on the studied phenomena as well as the use of SiNCs as a model platform for further study of the Stark effect in quantum confined structures as a whole.

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I. INTRODUCTION
The study of the red shift in the absorption/emission spectra of quantum confined structures due to an externally applied electric field, termed the quantum confined Stark Effect (QCSE), has, to a large extent, been limited to III-V structures due to their direct bandgap. For optoelectronic applications, the integration of devices into Si based CMOS integrated circuits is greatly beneficial as this would allow for faster high bandwidth interconnects. While III-V quantum wells can be successfully integrated into Si wafers, this is no trivial task. The use of different substrates necessitates processes such as epitaxial growth or wafer bonding. Alternatively, Ge-Si optical modulators based on QCSE on Ge quantum wells as well as the Franz-Keldysh effect on bulk Ge-Si have been reported, allowing for designs with better compatibility. From this perspective of process integration, Si–SiO$_2$ structures that do not require the use of different substrates can still offer unique benefits for the combination of opto-electronic elements with CMOS technology. There have been publications about the QCSE on Si structures. Kulakci et al. have successfully shown wavelength modulation due to the QCSE on Si nanocrystals (NCs) produced by ion implantation both at room temperature and at cryogenic temperatures, where the effect was more enhanced. While a change in emission intensity was reported in this study, it differs from other studies like that published by Lacombe et al. in the key aspect that the intensity modulation is a side effect rather than the main goal of a proposed optical wavelength modulator device. However, until now, there were no studies where the QCSE was analyzed as a function of the nanocrystal size which can be controlled through the constraint of the NC growth using the superlattice sedimentation method.

While NC size can also be controlled with solution-based methods, solid state growth processes provide unique benefits. Si nanocrystals (SiNCs) fabricated through the superlattice sedimentation method used in this study, where the growth of the crystals occurs already inside the oxide, do not require further steps to protect them from degradation due to oxidation, like quantum dots synthesized from solution. Another major advantage of the superlattice approach is the ability to constrain the mean size of the NCs along the axis of layer deposition, allowing for another degree of freedom in the tailoring of the bandgap for the intended purpose.
In our investigation, we have studied the effect of the NC size on the Stark shift observed in the emission spectra.

II. EXPERIMENTAL DETAILS

A series of size-controlled SiNC samples were prepared by depositing silicon-rich-oxide layers ($\text{SiO}_{x}\text{N}_{y}$) of defined thicknesses (2 nm–5 nm) between two 10 nm layers of stoichiometric $\text{SiO}_2$ on p-type Si wafers by plasma enhanced chemical vapor deposition (PECVD). An additional sample with a 20 nm silicon-rich-oxide layer was also fabricated as an example of an unconstrained-size control. The deposited layers were later annealed for 60 min at 1150 °C in an inert atmosphere so that the SiNCs are grown, and the dangling bonds were passivated in a $\text{H}_2/\text{N}_2$ atmosphere for 60 min at 450 °C. The silicon-rich-oxide layer thicknesses set the upper size limit to which the NCs can grow since the stoichiometric oxide layers on the top and at the bottom do not have excess silicon for continuation of the crystal growth. It is important to note that the PECVD thin film thicknesses were determined by repeating the individual deposition steps several times on calibration samples and measuring the total thickness by ellipsometry. The reported layer thicknesses are mean values without taken the roughness into account.

300 nm of $\text{ZnO}$ deposited by atomic layer deposition was used as the transparent front contact while evaporated Al layers of 300 nm were used for the back side. A DC bias voltage in the forward (accumulation) direction was applied to the contacts to generate the external field on the NCs. It was assumed that the entire voltage drop was limited to the oxide, and the field values in the Results section were calculated by modeling the NCs as a continuous layer of Si in the middle of two stoichiometric $\text{SiO}_2$ layers of equal thickness. Each sample contains a stack of only two oxide layers and a single SiNC layer. SiNC based multi-layer light emitting devices (LEDs) using the superlattice sedimentation approach were shown in the past to be a suitable platform as the turn-on voltages for these structures are lower than those of single layer SiNC LEDs. With the single layers sandwiched between thicker oxide barriers, the elimination of any contribution from electroluminescence in the photoluminescence (PL) spectra was aimed. This was also confirmed by spectroscopy measurements without excitation.

The QCSE on the respective sample spectra was characterized by PL spectroscopy measurements. The samples were cooled to 80 K in a vacuum cryostat using liquid nitrogen prior to being excited by a 325 nm CW He–Cd laser with a power density of $13.09 \times 10^{-4}$ mW m$^{-2}$. All measurements were performed under steady state conditions.

III. RESULTS AND DISCUSSION

The PL spectra shown in Fig. 1 for the size-controlled SiNCs without the external electric field serve as a reference point. The emission peak centers along the energy axis move toward higher values as the NC layer thickness is decreased from 5 nm (1.36 eV) to 2 nm (1.59 eV). This size dependent bandgap broadening is a result of quantum confinement in nanoscale silicon. Results shown in Fig. 1 are in agreement with previously published studies on low temperature luminescence properties of size controlled SiNCs.

It is also seen that the emission peak of the control sample is much wider than the samples with controlled growth. This is due to the control sample having an ensemble of NCs with a much broader size distribution. It is also important to note that only the mean size of the NCs along the direction of the layer deposition is constrained through the process. As deduced from the emission peaks, the NCs in the different samples composed of different layers show an overlap of their size distributions but different mean values. HRTEM analyses of samples prepared using the same process were reported in the past, showing continued growth and nucleation under the effect of the electron beam which results in difficulty in accurate size determination. For the purpose of this study, only the size constraint in the direction of the electric field is considered.

Under the effect of the applied potential, a red shift in the emission spectra was observed for all samples. As shown in Fig. 2, all acquired spectra for the 3 nm sample are shown as an example case where a maximum red shift from 1.49 eV at 0 V to 1.39 eV at 32 V is observed. Importantly, the emission peaks of several red shifted spectra lie partially outside the bounds of the 0 V peak, meaning that the observed phenomenon cannot be explained by selective quenching of the luminescence peak alone.

A shift in the energies of the electron and hole states in the NCs is caused by the external electric field induced by the bias voltage. Electron states can exist in a quantum confined structure, where otherwise, the electron and hole would get separated due to the shift in energy states under the effect of the electric field being greater than the binding energy of the electron–hole pair. This allows for the QCSE to be induced under much greater field magnitudes relative to bulk material. Since the shift in the energies of the electron and hole states will be in opposite directions, the shift in the energy of the emission peak due to the Stark effect can only ever be in the negative direction. It is also important to note that the red shift is accompanied by a decrease in the overall PL intensity. In the case of QCSE, the spatial overlap of the electron and hole wavefunctions within the NC is reduced due to the additional separation caused by the field, and this,
in turn, reduces the internal quantum yield.\textsuperscript{18} It was also suggested that a decrease in PL intensity accompanied with a red shift could be caused by the selective quenching of the PL where the Auger recombination rate is much higher for smaller NCs than larger ones. This would reduce the overall PL intensity but reduce the intensity of shorter wavelength emission more than longer wavelength emission.\textsuperscript{19} However, in the case where the red shifted spectrum of a sample lies outside the range of that of the same sample without any applied field, the peak shift cannot be explained by the selective Auger quenching mechanism alone. Our measurements were repeated in reverse (i.e., in the order of increasing voltage and then decreasing voltage), and the reduction in both the PL intensities and the red shift was confirmed to be reversible.

Figure 3 shows that the red shift due to the QCSE scales non-linearly with the field magnitude for all samples. This quasi-quadratic dependency on the field is a well-known property of the QCSE shown previously on III-V quantum dots and also on nanoscale Si in thermal oxide deposited through ion implantation without size control.\textsuperscript{9}

As can be clearly seen here for our well controlled samples, the extent of the shift in the emission spectrum caused by the QCSE depends highly on the layer size for the size-controlled samples, which is the equivalent parameter limiting the size to which the NCs can grow. One can clearly say that for the same field magnitude, there is a trend of decreasing red shift as the NC size gets smaller. However, since higher field magnitudes can be achieved at the same bias voltage using thinner samples, one must note that the samples with smaller NCs exhibit the highest red shift when compared at the same bias voltage. The unconstrained-size control sample with a layer thickness of 20 nm shows the highest amount of red shift. While this sample is not size-controlled, it still hosts an ensemble of Si NCs, albeit with a much broader size distribution. One can extrapolate from the trend of the size dependency of the QCSE that the mean size of the ensemble in the 20 nm control sample is larger than it is in all our other samples.

For a quantitative analysis of the trend shown in Fig. 3, we employ a simplified model of the SiNC in the oxide matrix. The NCs are modeled as infinite potential wells along the height of the layer stack with width \(d\) (i.e., NC size), where the potential drop inside the NCs (\(-d/2 \leq x \leq +d/2\)) is considered negligible. The QCSE is approximated by the time independent perturbation theory approach with applied perturbation being the change in potential energy due to the field along the vertical axis (\(eFx\)),\textsuperscript{20}

\[
(H_0 + eFx) \Psi_n^0 = E \Psi_n^0, \quad (1)
\]

where \(H_0\) is the Hamiltonian of the unperturbed system, \(e\) is the elementary charge, and \(\Psi_n^0\) is the wavefunction without the field of the form

\[
\Psi_n^0 = \sqrt{\frac{2}{d}} \sin \left( \frac{n \pi (x + d/2)}{d} \right). \quad (2)
\]

Applying the first and second order corrections, a quadratic relation between the field magnitude and the red shift is obtained,

\[
\Delta E = \frac{512 (m_e^* + m_h^*) e^2 F^2 d^4}{243 \pi^6 \hbar^2}, \quad (3)
\]

where \(m_e^*\) and \(m_h^*\) are the effective masses of the electrons and holes, respectively, and \(d\) is the width of the well (i.e., NC size along the x direction).\textsuperscript{21} This approximation, however, does not account for the shift induced by the field acting on whatever permanent dipole there

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**Figure 2.** PL spectra of the 3 nm sample at 80 K with a forward bias of up to 32 V DC. The dashed line is just to guide the eye marking the spectra in the order of increasing bias voltage.

**Figure 3.** Red shift analyzed using PL spectra of samples with different NC layer sizes plotted against the calculated field magnitudes, along with the 20 nm thick sample having no size control. The lines in the figure are obtained by the model using the corresponding fit parameters summarized in Table I.
might be present in the NCs without polarization. To account for that, a linear term is introduced,

$$\Delta E = \frac{512 (m_s + m_p) e^2 d^4}{243 \pi^2 \hbar^2} + m F,$$

(4)

where $m$ is the displacement vector for the dipole ($r$) multiplied by the elementary charge ($e$).

The fit curves for the experimental results are plotted as shown in Fig. 3 with the parameters listed in Table I. Even though the NC sizes obtained through the fit are larger than the layer the nominal layer thickness, the absolute discrepancy between the two values is less than 0.5 nm across the board. This level of predictability shows that the observed red shift in the emission peaks can, to a large extent, be explained by the change in the energies of the electron and hole states of the polarized NCs. However, when only the perturbation theory approximation was used to model the system, the modeled data did not fit the experimental results with any reasonable degree of accuracy; therefore, the built-in dipole moment of the NCs had to be taken into account, and the linear term was introduced. For the case where the studied NCs are spherical, it is reasonable to expect this term to be negligible. However, as it was shown in studies involving atom probe tomography on SiNCs prepared by the superlattice method, these NCs can have varied three-dimensional shapes.22

Another consistent trend is the increase in the built-in dipole displacement vector ($r$) with increasing NC size. As it is evident in Table I, the magnitudes of $r$ are significantly smaller than the NC sizes but show a clear increase with increasing NC size. Values for the dipole displacement vector similar to the findings in this paper, i.e., significantly lower than the mean NC size, have been reported previously for a Si–SiO$_2$ system.4 Aside from simply being an inaccuracy of the model due to the simplifications that were made, the magnitudes of these $r$ values may indicate the presence of interface dipoles.23 To that end, it is important to mention that with the H$_2$/N$_2$ passivation step, Si–H bonds are inevitably introduced at the Si–SiO$_2$ interface, neutralizing interface defects states which would otherwise result in "dark" nanocrystals. One could also argue that there might be a carrier migration between the neighboring NCs creating higher order effects that would cause discrepancy between modeled and experimental values. While this would have to be considered as a possible mechanism at room temperature, for 80 K, one would not expect this to happen since the energies would be too low for the transfer of carriers.

One of the greatest challenges for infrared photon detection is the material platform for the absorption of low energy photons. Being able to reduce the bandgap energy of Si through a low-power mechanism presents a unique method for device design. However, to fully exploit this potential, further research is necessary to investigate the QCSE on these structures at room temperature. Due to the high degree of accuracy that can be achieved with the SiNCs fabricated by this method and the relative simplicity with which the QCSE can be modeled to a reasonably high degree of accuracy, size-controlled SiNCs fabricated using the superlattice approach present a versatile model platform for further study of the QCSE in quantum well structures as a whole.

Overall, our study shows that both the magnitude of the red shift due to the QCSE and the dipole separation increase as the SiNCs get larger. This dependency can be reliably predicted by modeling the charge carriers as particles in a potential well and factoring in the built-in dipole moment on the NCs. We propose that bandgap energy modulated SiNCs can be used in infrared sensing applications due to their ability to reduce the bandgap energy. In addition, since the QCSE induced red shift does not require any current, this could provide the unique benefit of low power consumption in bandgap energy modulation.

### AUTHORS’ CONTRIBUTIONS

All authors conceived and planned the experiments. D.Y. carried out the experiments and wrote the manuscript with support from S.G. and M.Z.

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### DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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### TABLE I. Fit parameters and charge separation values for all samples. Nominal sample size values are the thicknesses of the NC layers deposited by the PECVD process.

| Sample | d (nm) | m (Cm) | r (nm) |
|--------|--------|--------|--------|
| 2 nm   | 2.14   | 4.47 × 10$^{-31}$ | 2.79 × 10$^{-5}$ |
| 2.5 nm | 2.70   | 5.53 × 10$^{-31}$ | 3.45 × 10$^{-5}$ |
| 2.75 nm| 2.99   | 5.98 × 10$^{-31}$ | 3.73 × 10$^{-5}$ |
| 3 nm   | 3.30   | 1.45 × 10$^{-30}$ | 9.05 × 10$^{-5}$ |
| 3.5 nm | 3.75   | 1.71 × 10$^{-30}$ | 1.07 × 10$^{-2}$ |
| 4 nm   | 4.32   | 2.16 × 10$^{-30}$ | 1.35 × 10$^{-2}$ |
| 5 nm   | 5.47   | 2.69 × 10$^{-30}$ | 1.68 × 10$^{-2}$ |
| Control| 8.15   | 3.78 × 10$^{-30}$ | 2.36 × 10$^{-2}$ |
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