Enhancement of the 1.54 μm Er^{3+} emission from quasiperiodic plasmonic arrays

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Periodic and Fibonacci Au nanoparticle arrays of varying interparticle separations were fabricated on light emitting Er:SiN_x films using electron beam lithography. A 3.6 times enhancement of the photoluminescence (PL) intensity accompanied by a reduction in the Er^{3+} emission lifetime at 1.54 μm has been observed in Fibonacci quasiperiodic arrays and explained with radiating plasmon theory. Our results are further supported by transmission measurements through the Fibonacci and periodic nanoparticle arrays with interparticle separation in the 25–500 nm range. This work demonstrates the potential of quasiperiodic nanoparticle arrays for the engineering of light emitting devices based on the silicon technology.
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Erbium-doped materials have recently emerged at the forefront of silicon photonics due to their potential for the engineering of on-chip light sources and laser structures operating at 1.54 μm. Recently, efficient Er^{3+} excitation and intense photoluminescence (PL) have been observed at room temperature in Er:SiN_x, which is an emerging Si-compatible material platform ideally suited for the fabrication of high-quality photonic/plasmonic structures and electrically pumped devices.[1,2] However, the small radiation rate of Er^{3+} ions unfavorably competes with more efficient nonradiative de-excitation paths, such as cooperative upconversion[3] and concentration quenching,[4] which become dominant at the high Er concentrations needed to engineer significant gain for on-chip applications.

In this letter, we demonstrate PL and radiative rate enhancement of Er^{3+} ions in a SiN_x matrix by coupling the Er^{3+} emission to localized surface plasmons (LSPs) modes in strongly scattering quasiperiodic Fibonacci arrays of Au nanocylinders.

LSP are collective oscillations of conduction electrons in metal nanoparticles coupled to electromagnetic waves. LSP have been extensively investigated for a wide range of applications, including radiative rate engineering, optical biosensing, and subwavelength light transport, owing to their ability to significantly enhance optical cross-sections and electromagnetic field intensities around metal nanoparticles.[5,6] In particular, the excitation of LSP modes can increase the emission rate of optically active dipoles by a combination of two following factors: (i) an enhancement of the dipole excitation rates due to high-intensity localized pump fields[5,6] and (ii) a modification of the local density of states (LDOS) at the emission wavelength which affects the radiative properties of emitting dipoles via the interaction with metals.[7–10] An emitting dipole positioned in the proximity of a metal nanoparticle system decays nonradiatively, on a fast time scale, by coupling into the LSP modes of the system. Subsequently, the LSP modes can decay (out-couple) into radiative photonic modes or nonradiative loss channels, depending on the ratio of the scattering/extinction efficiencies (albedo) of the plasmonic system at the emission wavelengths. For optimum radiative enhancement, the geometry of the system should be designed to facilitate maximum nonradiative transfer of energy to the LSP modes and simultaneously the albedo has to be optimized for efficient out-coupling of the LSP energy into far-field radiation by engineering the particle and array morphologies.

Considerable amount of work has already been done on this front using periodic nanoparticle arrays with varied particle shapes, sizes and interparticle[11,12] distances. However, a careful study of the role of the array geometry is still missing. We have previously investigated the geometry-dependent optical properties of LSP modes in deterministic aperiodic arrays and demonstrated broadband plasmonic activity[13,14] along with spatially averaged surface enhanced Raman scattering enhancements up to 10^8 using Fibonacci arrays of Au nanoparticles.[15,16] The unique optical properties of Fibonacci nanoparticle arrays, which originate from the excitation of multiple photonic-plasmonic hybrid modes,[13] make these systems particularly attractive for radiative rate engineering applications.

In order to investigate the emission properties of plasmon-coupled quasiperiodic systems, an Er:SiN_x film of approximately 100 nm thickness (refractive index=2.05 @ 1550 nm) was fabricated on quartz wafers using N_2 reactive magnetron cosputtering with Si and Er targets.[1] Subsequently, periodic and Fibonacci nanoparticle arrays with minimum interparticle separation (edge to edge) Δ_{min} ranging from 25 to 500 nm were fabricated on the same chip by the process described in Refs. 13–15. The scanning electron micrographs and AFM images in Figs. 1(a)–1(c) show two representative arrays of nanoparticles with 100 nm radius, 30 nm thickness, and the $\Delta_{min}=25$ nm.

The geometry-dependent resonant frequencies of periodic and Fibonacci arrays were experimentally identified in a transmission experiment by the spectral positions of the transmission minima.[11,12] The transmission measurements were carried out under illumination through a 60× objective (numerical aperture, NA=0.8), and the transmitted light was collected with a 10× objective (NA=0.15). The transmit-

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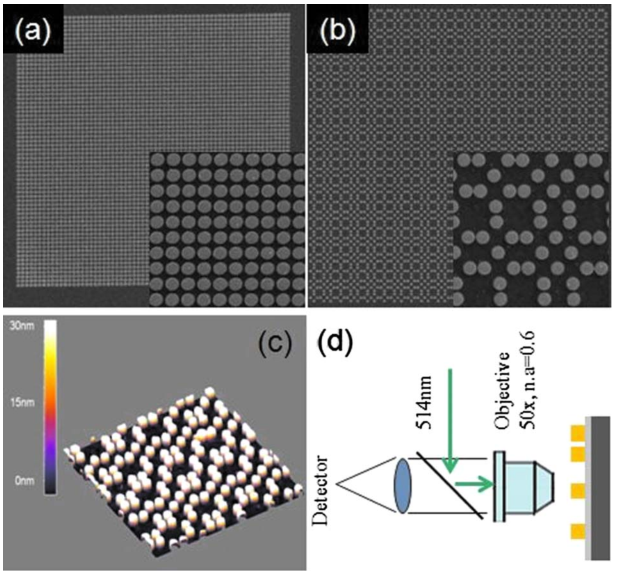

FIG. 1. (Color online) SEM micrograph of (a) periodic, (b) Fibonacci array Au nanocylinders with r=100 nm, and Δ_{min}=25 nm. (c) AFM of Fibonacci nanoparticle array. (d) The experimental setup for PL measurements.

tance through each of the arrays was normalized by the transmission through an adjacent unpatterned area of the samples.

The experimentally measured transmission data are shown in Fig. 2, which features the wavelength dependent photonic-plasmonic resonances in the periodic and Fibonacci nanoparticle arrays. The transmission spectra of the periodic arrays exhibit a clear dip which redshifts with increasing Δ_{min} in agreement with previous results.[5,6] On the other hand, for the Fibonacci arrays a transmission dip is observed at 1.54 μm irrespective of the Δ_{min}. This behavior reflects the unique transmission characteristics of multiscale quasiperiodic arrays, which feature spectrally overlapping photonic-plasmonic resonances forming frequency bands which are relatively insensitive to variations in Δ_{min}.[13] These scattering resonances of the Fibonacci arrays have been observed in the visible and are more pronounced in the near infrared (NIR) due to the reduced extinction losses.

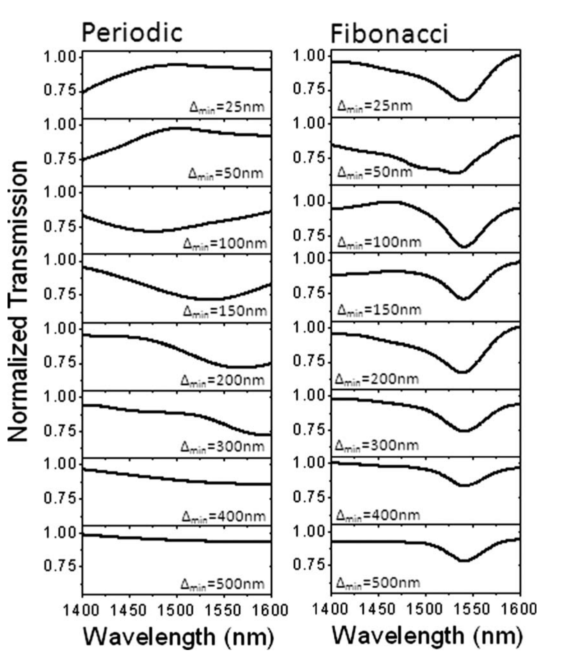

FIG. 2. Normalized transmission spectra of periodic and Fibonacci Au nanoparticle arrays with specified interparticle separations Δ_{min}.

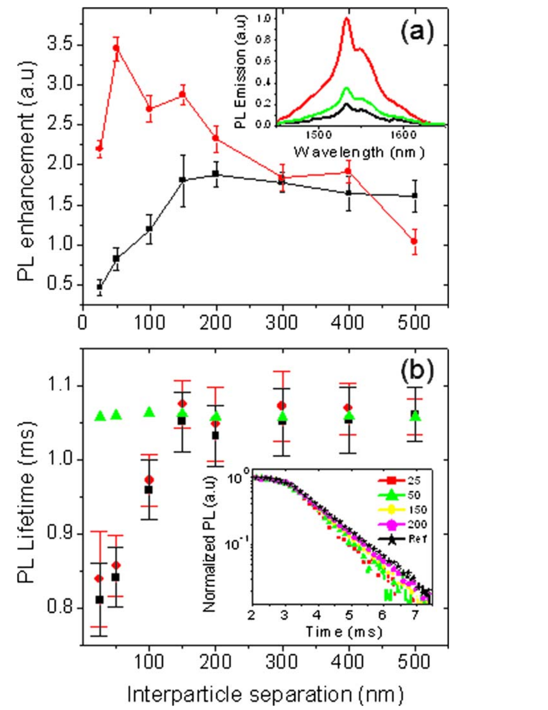

FIG. 3. (Color online) (a) Integrated PL enhancement in periodic (circle) and Fibonacci (square) nanoparticle arrays of various interparticle separations. The inset shows the representative PL spectrum of periodic (bottom), Fibonacci (top) nanoparticle arrays with Δ_{min}=50 nm and unpatterned area (middle). (b) PL lifetime of periodic (circle), Fibonacci (square), unpatterned (triangle). Inset Er decay of unpatterned (star) and Fibonacci arrays with different Δ_{min} as specified in the legend.

In order to understand the role of Fibonacci quasiperiodicity in the Er^{3+} emission, the Er PL intensity and its decay dynamics were measured at room temperature under excitation from the 514 nm line of an Ar ion laser (Spectra Physics, 177–602) and detected using liquid N_2 cooled extended photomultiplier tube (Hamamatsu R5509–73) detector. The schematic of the PL measurement setup is shown in Fig. 1(d) as follows: the excitation laser was focused through a 50× microscope objective and a long-pass filter (absorbing wavelengths below 1300 nm) was used to reject the incident laser light as well as the visible PL emission from the Er:SiN_x. The Er^{3+} PL enhancement was quantified by measuring the ratio of the PL through each array against the PL from the adjacent unpatterned areas. Figure 3(a) shows the integrated Er^{3+} PL intensity enhancement through the periodic (black) and Fibonacci (red) nanoparticle arrays with different Δ_{min} [In Figs. 3(a) and 3(b) the error bars were quantified from six distinct measurements over two independently fabricated samples]. Representative PL spectra obtained from periodic and Fibonacci nanoparticle arrays with Δ_{min}=50 nm and from the adjacent unpatterned areas are shown in the inset of Fig. 3(a). The emission enhancement observed in periodic array of Au nanocylinders peaks at Δ_{min}=150–200 nm, corresponding to the maximum spectral overlap between the transmission dip and the Er emission spectrum (Fig. 2), in agreement with previous observations.[11] However, further reduction in Δ_{min} results in a dramatic drop in the PL intensity due to the increased metallic losses accompanied by the gradual detuning of the transmission modes with the Er emission. In the case of Fibonacci arrays, we observed a maximum emission enhancement at Δ_{min}=50 nm. This behavior is especially interesting since the transmission spectra of Fibonacci arrays do not significantly shift with varying $\Delta_{\min}$. The result suggests that a simple overlap of transmission dip with the PL emission band is not enough to ensure optimum PL enhancement. In fact, in addition to the transmission characteristics, which reflect far-field properties of the arrays, the spatial overlap of the electromagnetic near-field modes at the emission wavelength with the emitters also plays a crucial role[17] in the emission enhancement process. In an effort to understand the contribution of the pump on the PL enhancement, we measured the transmission characteristics of the samples in the visible spectral range. The normalized transmission at the pump wavelength (514 nm) was found to increase by 10% and 8% for Fibonacci and periodic arrays, respectively, with increasing $\Delta_{\min}$. This small change in pump transmission is insufficient to explain the large variation in the observed PL intensity.

In order to understand the origin of the Er PL enhancement we have studied the PL decay dynamics. Figure 3(b) shows the PL decay time through the periodic and Fibonacci nanoparticle arrays by varying $\Delta_{\min}$. We observed that the PL lifetime reduces significantly by decreasing $\Delta_{\min}$ for both periodic and Fibonacci nanoparticle arrays, while retaining an almost single exponential decay character.[7–9] A similar reduction in the single exponential Er emission lifetime has been observed in previous studies and explained by plasmon-enhanced radiative rate[7,8,18–20] (LDOS modifications), which are more pronounced for small $\Delta_{\min}$.[17]

Our experimental results can also be qualitatively explained in the context of the radiating plasmon theory[10] as follows. The emitting Er dipole initially transfers its energy into a plasmonic mode, which can subsequently decay nonradiatively by heat generation into the metal or radiatively by releasing energy into the far-field depending on the albedo of the nanoparticle arrays. Specifically, for a system of identical dipoles in the presence of a plasmonic array, the total emission intensity I_T can be written as follows:[10]

$$I_T = I_E + I_{LSP} \propto I_p \eta_p \eta_0 (1 - \eta_{LSP}) + I_p \eta_p \eta_0 \eta_{LSP} Q_{scatt}, \quad (1)$$

where I_E ($I_E \propto I_p \eta_p \eta_0$) is the contribution from dipoles uncoupled to the metal, I_{LSP} ($I_{LSP} \propto I_p \eta_p \eta_{LSP} Q_{scatt}$) is the plasmon enhanced emission from coupled dipoles, I_P is the pump intensity, η_p is the pump efficiency, η_0 is the internal quantum efficiency of the emitter, η_{LSP} is the efficiency of the energy transfer (nonradiative) to LSP modes, Q_{scatt} is scattering efficiency of the plasmon array at the emission wavelength. The coupling efficiency η_{LSP} is defined as follows:

$$\eta_{LSP} = \frac{\Gamma_{LSP}}{\Gamma_{rad} + \Gamma_{non\ rad} + \Gamma_{LSP}}, \quad (2)$$

where Γ_{rad} and Γ_{nonrad} are the intrinsic radiative and nonradiative decay rates of the emitter and Γ_{LSP} is the energy transfer rate into the LSP mode.[7,8,10]

Since in our experimental conditions η_p remains approximately constant for the different arrays under consideration, the observed PL intensity enhancement I_T/I_E is determined by both η_{LSP} and Q_{scatt} through the following relation:

$$\frac{I_T}{I_E} \propto (1 - \eta_{LSP}) + \eta_{LSP} Q_{scatt}. \quad (3)$$

In the case of periodic nanoparticle arrays η_{LSP} increases with decreasing $\Delta_{\min}$ due to the stronger coupling to LSP modes, leading to a reduction in the measured decay time. Simultaneously, the detuning of the far field scattering spectra with respect to the emission wavelength (Fig. 2) reduces Q_{scatt} and the PL intensity. On the other hand, for Fibonacci nanoparticle arrays, the strongly reduced frequency sensitivity of photonic-plasmonic scattering resonances prevents their detuning from the Er emission wavelength. As a result, when decreasing $\Delta_{\min}$, the PL intensity of Fibonacci arrays increases with a simultaneous reduction in its decay time.

In conclusion, we have investigated Er PL enhancement in periodic and quasiperiodic Fibonacci arrays of Au nanocylinders with various interparticle separations fabricated on $Er:SiN_x$ films. We observed up to 3.6 times increase in the PL emission intensity accompanied by a 34% ± 16% change in the PL decay lifetime in the case of Fibonacci arrays. Further increase in the PL intensity can be achieved by enhancing the excitation rates in engineered nanoparticle arrays[21,22] that additionally support high-intensity localized electromagnetic fields at the pump wavelength,[5,6] which is the subject of our future studies.

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