Tunable Optical Properties and Recombination Dynamics of $Ge_{1-x-y}Si_ySn_x$ Nanoalloys

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Abstract: We report on quantum confined $Ge_{1-x-y}Si_ySn_x$ nanocrystals demonstrating both size- and composition-tunable direct visible/NIR emission (1.77 – 2.47 eV) and recombination dynamics. Temperature-dependent time-resolved photoluminescence suggests significant enhancement of oscillator strengths with Si incorporation.

1. Introduction

Group IV materials (namely Si and Ge) remain at the forefront of semiconductor technology, underpinning a majority of the electronic devices presently in use and exhibiting numerous desirable traits such as nontoxicity, wide-ranging compatibility, and high elemental abundance. Optical performance, however, is fundamentally hindered by inherent indirect band structures, resulting in highly inefficient light-matter interactions compared to their direct-gap counterparts. To overcome these restrictions, we have utilized a combination of quantum confinement and compositional modification, synthesizing purely-Group IV colloidal $Ge_{1-x-y}Si_ySn_x$ nanocrystals (NCs) exhibiting homogenous ternary-alloy crystalline structures, direct gaps, and size- and composition-based emission tunability in a wide spectral range. These favorable properties magnify their potential for implementation in Si-compatible photonics applications, for example, acting as highly-efficient Group IV light emitters/detectors, nontoxic biological imaging agents, or as augmentation for on-chip quantum communications and related devices.

2. Group IV Nanostructures

2.1 Background

With structural and compositional modification, the usability of Group IV materials can be significantly expanded. At sufficiently small crystallite sizes, quantum confinement has been demonstrated to induce significant modification of band structures, pushing optical transitions towards the quasi-direct regime and providing a limited range of size-tunable emission within the visible/NIR [1]. Similarly, admixture of α-Sn into Si and Ge nanostructures additionally promotes this direct gap behavior even in bulk form and significantly enhances the oscillator strengths of associated optical transitions, stemming from the resulting expansion of the Si/Ge lattice [2]. The relatively small energy gap of α-Sn (E_g = 0.08 eV), though, necessitates the inclusion of Si in the ensuing alloy if any potential in the visible to NIR range is to be retained. This is further restricted by the thermodynamic instability of Si-based alloys containing >~10% Sn, greatly reducing the probability of obtaining bulk homogenous alloys in practice. In contrast, the large surface-to-volume ratio and degree of curvature of colloidal NCs allow for structural relaxation which reduces the strain from inhomogeneities within the lattice. This permits a wider range of stable alloy compositions to be synthesized and thus additional energy gap tunability via varying contents of both Si and Sn [3,4].

2.2 Binary and Ternary Structures

While SiGe alloys have been extensively characterized, the behavioral basis for Sn inclusion into alloy NCs has been only recently been demonstrated. Our colloidal synthesis of $Ge_{1-x}Sn_x$ binary-alloy NCs over a wide range of Sn compositions (x = ~0-30%) has produced homogeneous quantum-confined nanostructures for a wide range of diameters (1.8-5.9 nm). This combined influence of varying Sn inclusion and confinement resulted in fundamental core-related PL emission with tunability between 2.01-1.31 eV; consistently redshifting with increasing Sn and/or nanocrystal diameter [2,5]. Although spanning much of the visible to NIR in accordance with trends suggested by theory, the quasi-direct transition associated fast (~ns) decays were present only near room temperature. At 15K, time constants increased by multiple orders of magnitude, with the dramatic shift to ~μs decays attributed to dark-bright exciton splitting in which the reduction in thermal energy makes the "bright" fast excitonic states inaccessible, confining carriers to slow spin-forbidden "dark" states. Only with large Sn content (>~20%) is this effect reduced, limiting potential spectral tunability by this parameter alone [2].

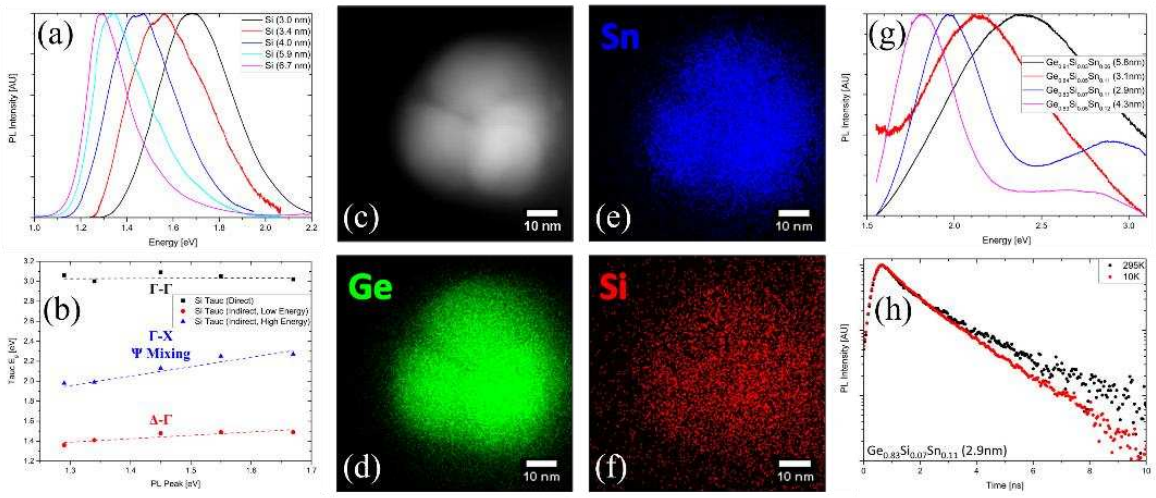

Fig. 1. (a) Size-tunable PL spectra of Si NCs. (b) Dependence of Si NC Tauc energy gaps on PL peak energy. (c-f) Dark field STEM image and STEM-HAADF elemental maps for $Ge_{0.84}Si_{0.07}Sn_{0.09}$ NCs showing homogenous alloy formation. (g) Room-temperature PL spectra for GeSiSn NCs. (h) TRPL transients for $Ge_{0.83}Si_{0.07}Sn_{0.11}$ NC sample measured at 295K (black) and 15K (red).

By themselves, pure Si NCs clearly display size-tunable emission across the visible/NIR, as presented in Fig. 1a. When compared to Tauc gaps, however, distinct *apparent* energy shifts occur between PL peaks and the absorption critical points, with the associated direct/indirect transitions as typically ascribed being noted in Fig. 1b [1]. Thus, the combined inclusion of both Si and Sn expands the exploration potential of these structures and their associated recombination dynamics while retaining wide spectral tunability. Experimental synthesis of colloidal $Ge_{1-x-y}Si_ySn_x$ NCs has been recently reported, being comprised of homogenous Ge, Sn (x = 1.8-6.4%), and Si (y = 0.9-16.1%) alloys such as that illustrated via STEM in Fig. 1c-f [4]. This range has since been extended to systematically probe energy gap modification, encompassing Sn compositions up to 17.9%. As shown in Fig. 1g, such subsequently fabricated NCs (2.9 – 5.8 nm) display prominent PL peaks tunable throughout the visible spectrum, constituting a substantial expansion of the spectral range attainable with this class of nanostructures. In contrast to $Ge_{1-x}Sn_x$ NCs and the temperature-independent long indirect gap transients observed in typical Si and Ge NCs [1,2], the increased affinity for long recombination at low temperatures has not been observed. Time constants consistently remain in the low-ns range at all measured temperatures (displayed in Fig. 1h), diameters, and substantial Si/Sn inclusion levels. This appears to indicate an inherent direct transition fundamental to the $Ge_{1-x-y}Si_ySn_x$ ternary-alloy confined system, with significant modification of band structure dependent on both Si and Sn composition.

3. Conclusion

Within this work, we demonstrate that the utility of Group IV nanostructures in optoelectronic implementations can be greatly expanded with the introduction of $Ge_{1-x-y}Si_ySn_x$ nanoalloys; allowing for direct energy gaps widely tunable across the visible to NIR via both size and multi-elemental composition while still retaining desirable implementation properties. Additionally, the limitations in achievability of desirable energy gaps and room-temperature thermodynamic stability present in related binary alloys and bulk nanocrystals are shown to be overcome both by the ternary-alloy combination of Ge, Si, and Sn and quantum confinement, eliminating many traditional concerns. We will report on a systematic study to establish the extremes of compositional- and confinement-based tunability, along with the associated band structure modifications evident by α-Sn/Si inclusion.

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4. References

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