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# Quantum confinement in mixed phase silicon thin films grown by co-deposition plasma processing



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## ABSTRACT

Mixed phase, hydrogenated amorphous and nanocrystalline silicon thin films grown by co-deposition (nanocrystals and amorphous material deposited sequentially in the same vacuum system) demonstrate pronounced quantum confinement effects. Based on photoluminescence measurements of co-deposited samples, we find evidence that the optical gap of nanocrystals embedded in hydrogenated amorphous silicon is increased to energies exceeding bulk crystalline silicon values – at least as high as 1.35 eV. The broad spectrum of emission of the nanocrystals is attributed to the size distribution and local fluctuations in matrix hydrogenation. The temperature dependence of this PL suggests that these nanocrystals possess fewer defects than those grown by conventional plasma enhanced chemical vapor deposition methods. Interactions between electronic states in nanocrystals and localized states in amorphous silicon matrix tissues are discussed in terms of their role in determining the strength of the quantum confinement potential.

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## 1. Introduction

Mixed phase, hydrogenated amorphous and nanocrystalline silicon (a/nc-Si:H) is a technologically relevant nano-material with applications extending from thin film transistors to solar panels. It is composed of silicon nanocrystals (ncs) in a hydrogenated amorphous silicon (a-Si:H) matrix, and is typically synthesized using a plasma enhanced chemical vapor deposition (PECVD) process in which the ncs and a-Si:H tissues form simultaneously and the hydrogen dilution is modified throughout the growth process to maintain the nanocrystal size and volume fraction constant throughout the thickness of the film [1]. A second standard way of making a/nc-Si:H is to modulate the hydrogen dilution [2]. Improvements in the stability and transport properties of a/nc-Si:H relative to a-Si:H alone indicate that the ncs play a central role in an improved set of electronic properties [3]. The mechanisms determining the microstructural evolution of conventional a/nc-Si:H, however, do not allow a great deal of control over the nc geometry or their interface with amorphous tissue. For example, as a consequence of the competing growth of crystalline

and amorphous phases, highly defective grain boundary domains form, wherein variations in bond length and angle at nc surfaces give rise to a distribution of shallow defects known as *band-tail* states [4,5]. In addition, the hydrogenation of grain surfaces, which passivates defects [6], is not directly accessible using conventional methods. Thus, better control of nc synthesis, and in particular access to the quantum confined (QC) nc regime to create higher band-gap materials, are both very desirable.

High quality PECVD grown a/nc-Si:H used for solar cells, which is the material employed in the present study, contains ncs averaging about 20 nm in length with 6 nm diameters [7], which are too large to exhibit significant QC. Recently, however, Bagolini et al. used low energy PECVD to synthesize a/nc-Si:H with nc diameters as small as 3.2 nm, and the photoluminescence (PL) of their films showed indications of QC [8]. This signified that it may be possible to design a/nc-Si:H using nc size to tune its optical properties. The present work builds on this result, focusing on the optoelectronic properties of a/nc-Si:H prepared by a specialized co-deposition process that decouples nc formation from a-Si:H matrix growth. This provides a high degree of control over nc properties and produces a/nc-Si:H materials with well pronounced QC. In addition, the co-deposition methodology confers other advantages. For example, results from PL experiments performed over a range of temperatures suggest ncs in co-deposited a/nc-Si:H possess fewer defects than ncs in a/nc-Si:H grown by conventional

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methods. This work demonstrates co-deposition as a viable and promising new approach for synthesizing high band-gap a/nc-Si:H, and points to unexplored opportunities for exploiting the unique properties of quantum confined nanoparticles in ordered/disordered paracrystalline systems.

## 2. Co-deposition synthesis of a/nc-Si:H

In the conventional process to make a/nc-Si:H,  $\text{SiH}_4$  and  $\text{H}_2$  gas precursors decompose in a capacitively coupled plasma reactor, and films with mixed phase microstructure result from competing growth between a-Si:H and nc domains [9]. On the contrary, the co-deposition process combines a unique, specialized, plasma-based nc synthesis technique with conventional PECVD growth of a-Si:H. In this case, nanocrystals form in the primary stage as  $\text{SiH}_4$  feed gas, heavily diluted with an inert carrier (typically argon), decomposes in a capacitively coupled, quartz tube, plasma reactor. This process has been extensively characterized and results in high quality, nearly spherical, crystalline nanoparticles with hydrogen-terminated surfaces [10,11]. Then the nanocrystals flow into a second, more conventional, capacitively coupled plasma reactor to become embedded in a growing a-Si:H film. This allows insertion of very small ncs into the a-Si:H matrix. Further details of the co-deposition method can be found in Refs. [10,12].

Transmission electron microscopy (TEM) results (Fig. 1) show characteristic cross-sections of conventional and co-deposited a/nc-Si:H samples. Comparing Fig. 1(a) and (b), we see crystalline

domains in co-deposited a/nc-Si:H are substantially smaller than in the conventional material. Fig. 1(c) shows a  $\sim 4$  nm diameter Si nc in the co-deposited film – well below the Bohr exciton radius for Si. From the histogram construct shown in (Fig. 1(d)), extracted by taking the diameter of all nc's imaged in co-deposited a/nc-Si:H, we find a mean diameter of 3.8 nm.

## 3. Comparing photoluminescence from co-deposited and conventional a/nc-Si:H distinguishes quantum confined Si nc emission in co-deposited material

Fig. 2 compares room temperature Raman and 20 K PL spectra of co-deposited and conventional PECVD grown a/nc-Si:H films. The crystalline volume fraction,  $X_c$ , values determined by decomposing the Raman spectra into amorphous and crystalline contributions [13] were 0.01, 0.05, and 0.10, for co-deposited a/nc-Si:H samples and  $X_c=0.40$  for the conventional a/nc-Si:H sample. More recent Raman decomposition schemes [14,15] will yield different absolute values but the trend will remain the same.

Emission profiles from conventional a/nc-Si:H (Fig. 2(b) – bottom) have peaks at  $\sim 1.40$  eV and  $\sim 0.90$  eV. The higher energy peak, seen when an appreciable a-Si:H volume fraction is present, arises from transitions between band-tail states [16,17]. The lower energy peak is observed when ncs are present, and its magnitude relative to the higher energy peak correlates with  $X_c$  [18]. We therefore know it is associated with the ncs. Since its energy is below that of the Si band-gap, we attribute this band to defect

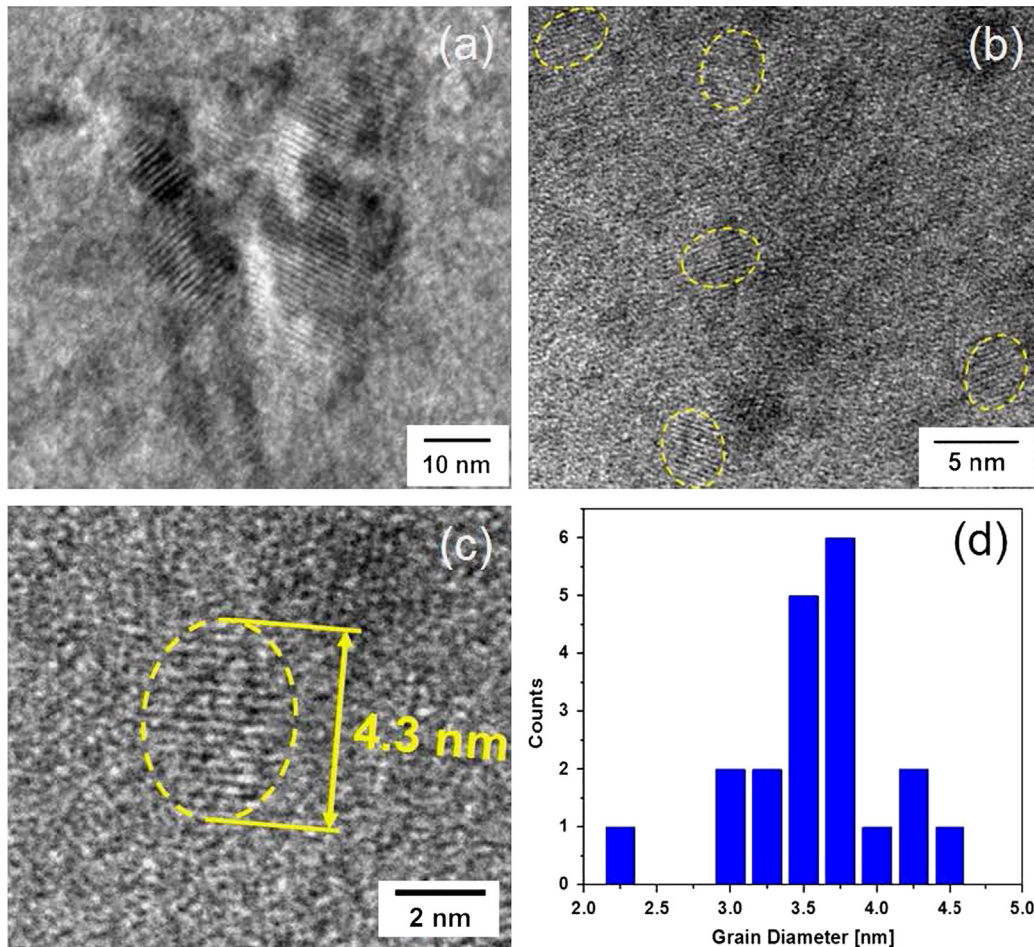


Fig. 1. High-resolution TEM images show cross-sections of (a) conventional, and (b) co-deposited a/nc-Si:H, (c) shows a Si nc with diameter of 4.3 nm embedded in a-Si:H tissues in co-deposited a/nc-Si:H, and (d) shows a nc diameter histogram for the co-deposited a/nc-Si:H, revealing the number of grains imaged with corresponding dimensions, and a characteristic size of  $\sim 3.8$  nm.

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