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Size-dependent spectral transmittance of crystalline silicon from bulk regimes to the quantum-confined

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It is necessary to distinguish between inherent changes in silicon's electrical structure and geometric size effects in order to comprehend the transition from bulk-like optical activity to quantum-confined behavior. Here, a size-dependent band-gap model, the Tauc relation, and the Beer-Lambert law are used to investigate the absorption coefficient and spectral transmittance over five size regimes ranging from 100 μm to 1 nm. The findings show that this evolution is governed by two different mechanisms. The absorption coefficient essentially stays bulk-like from the micrometer scale down to tens of nanometers, whereas transmittance gradually increases mostly due to the shorter optical path length. In the 1–10 nm regime, however, quantum confinement modifies the energy gap and absorption spectrum, making the optical response intrinsically size dependent. Comparison with available experimental and reference data shows good qualitative agreement in the spectral trends. The results therefore distinguish thickness-induced transmission enhancement from genuine quantum-confinement effects and provide a continuous framework for describing and tuning the optical response of silicon through dimensional control in photonic and optoelectronic applications.

Keywords: Quantum-confined; Spectral transmittance; c-Si regimes; SiQDs; Absorption Coefficient.

1. INTRODUCTION

Spectral transmittance is an important parameter for describing the wavelength-dependent optical response of crystalline silicon (c-Si), together with its absorption and reflection characteristics [1,2]. Reliable optical data for c-Si over approximately 250–1450 nm provide a fundamental basis for analyzing light propagation and optical losses, which are particularly important in photovoltaic applications [1–4]. Transmittance and absorption measurements also provide essential experimental information for modeling the interaction of silicon with electromagnetic radiation [2,5]. When the dimensions of silicon are reduced sufficiently to approach the relevant confinement scale, quantum confinement can modify its electronic structure and optical transitions, producing a size-dependent optical response [5–7]. In particular, Si quantum dots exhibit a blueshift of the absorption edge and optical transitions as their size decreases, with pronounced changes reported below approximately 6 nm [6,7]. Studies over broad wavelength ranges have also shown that the optical band gap increases with decreasing quantum-dot size [7]. Thus, spectral transmittance and absorption are important not only for understanding the transition from bulk to quantum-confined silicon but also for optimizing Si-based photovoltaic, photonic, photodetector, and optoelectronic applications [3–5].

Several studies have investigated the size-dependent optical properties of crystalline silicon nanocrystals. Wilcoxon et al. reported size-dependent absorption and direct/indirect transitions for 2–10 nm Si nanocrystals, with blueshifts at smaller sizes [8], while Kovalev et al. showed that Si nanocrystals can retain optical features similar to bulk Si despite quantum confinement [9]. Optical studies of Si nanocrystals in SiO_2 have also investigated nanocrystal sizes in the few-nanometer range [10]. Alonso et al. observed blueshifts in the dielectric function, absorption edge, and photoluminescence below approximately 6 nm, while larger nanocrystals retained more bulk-like optical characteristics [6]. Jia et al. found that the optical band gap increases with decreasing size over the investigated spectral range of 350–2500 nm [7], whereas Gresback et al. reported a blueshift of the lowest direct transition from 3.4 eV at 16 nm to 3.6 eV at 3.9 nm [11]. Ni et al. further highlighted the roles of size, surface, and doping in controlling the optical properties of Si nanocrystals [12].

This work systematically examines the size-dependent spectral transmittance of crystalline silicon from the bulk to the quantum-confined regime, taking into account characteristic dimensions ranging from 100 μm to 1 nm. The analysis covers five dimensional regimes: (100–10) μm, (10–1) μm, (1000–100) nm, (100–10) nm, and (10–1) nm. The study looks at how the spectrum transmittance and absorption coefficient change over various regimes and separates changes that are mostly due to shorter optical paths from those that are related to size-dependent electronic structure modification. From bulk dimensions to the quantum-confined realm, this method offers a continuous explanation of crystalline silicon's spectral response.

2. THEORETICAL MODEL

2.1 Crystalline silicon quantum dots' (SiQDs) size-dependent band-gap energy

Here, we examine the size-dependent optical properties of crystalline silicon (c-Si) in five useful dimensional regimes: Submicron Si (100–1000) nm, large-scale bulk c-Si (10–10) μm, bulk c-Si (1–10) μm, silicon nanoparticles/nanocrystals (10–100) nm, and silicon quantum dots (SiQDs) (1–10) nm. The latter two ranges fall within the nanoscale, which is approximately defined as 1–100 nm by ISO 80004-1:2023 [13]. Crystalline silicon nanocrystals with dimensions below approximately 10 nm are commonly discussed within the Si quantum-dot regime [5,12]. However, classification by dimensional

size does not imply equally strong quantum-confinement effects throughout the entire 1–10 nm range. Experimental studies indicate that pronounced quantum-confinement effects on the optical properties of Si nanocrystals become particularly evident at dimensions of only a few nanometers, with significant spectral changes reported below approximately 6 nm [6]. This classification therefore provides a practical framework for examining the evolution of silicon optical properties from bulk dimensions to the quantum-confined regime.

The size-dependent band-gap energy of crystalline silicon quantum dots (SiQDs) is estimated using the strong-confinement approximation [14]:

$$Eg\ (D) = Eg\ (bulk) + \frac{A}{D^{\delta}} \tag{1}$$

where $Eg(D)$ is the band-gap energy of a SiQD with diameter D. Eg bulk is the bulk silicon band-gap energy, and D is the quantum-dot diameter in nanometers. For the strong-confinement description adopted in the present calculations, (A=3.57) eV·nm² and (δ=2). Its D^{2}dependence is consistent with the strong-confinement treatment of silicon nanocrystals.

2.2 The absorption coefficient

The absorption coefficient is described using the generalized Tauc relation [15]:

$$(\alpha hv)^{\frac{1}{n}} = B\ (hv - Eg) \tag{2}$$

where α is the absorption coefficient, hv is the photon energy, Eg is the band-gap energy,B is a proportionality parameter, and n is an exponent determined by the assumed nature of the optical transition [15]. By introducing the size-dependent band-gap energy $Eg(D)$ obtained from Eq. (1) and using $hv = hc/\lambda$, the absorption coefficient can be expressed as a function of wavelength and quantum-dot diameter, α(λ,D) [14].

2.3 The spectral transmittance

The spectral transmittance of crystalline silicon is described by the Beer–Lambert law [2]:

$$T\ (\lambda.D\ .L) = exp\ (-\alpha(\lambda.D)\ L) \tag{3}$$

where T is the spectral transmittance, $\alpha(\lambda.D)$ is the wavelength- and size-dependent absorption coefficient, and L is the effective optical path length through the silicon structure. According to this relation, transmittance decreases exponentially as either the absorption coefficient or the optical path length increases [16]. Therefore, for a given absorption coefficient, reducing the propagation distance increases the transmitted fraction of the incident radiation.

The present Beer–Lambert treatment represents an idealized absorption-limited model. There is no specific mention of surface reflection, numerous internal reflections, thin-film interference, scattering, substrate effects, or surface/interface contributions. Therefore, while analyzing the discrepancies between the estimated and observed transmittance spectra, these effects are taken into account. The effective optical path length L is assumed to match the characteristic dimension assigned to each silicon structure under investigation for the comparison computations. This assumption allows for a

consistent analysis of the impact of dimensional reduction on spectral transmittance across the size regimes under consideration. The characteristic dimension ascribed to each silicon structure under investigation is used to approximate the effective optical path length L for the comparison computations. This approximation should not be construed as a general equivalency between particle size and optical path length; rather, it is used as a simplified modeling assumption to give a consistent basis for comparing the effect of dimensional reduction throughout the explored regimes.

3. RESULTS AND DISCUSSION

3.1 Size dependence of the spectral absorption coefficient

Figure1 shows the calculated absorption coefficient of crystalline silicon as a function of wavelength over the investigated dimensional regimes. Within the present model, the calculated absorption spectra for the (100–10) μm, (10–1) μm, (1000–100) nm, and (100–10) nm regimes overlap; therefore, only one representative curve is presented in Figure1(a) to avoid redundant presentation. In contrast, the (10–1) nm regime exhibits a distinct size-dependent absorption behavior and is presented separately in Figure 1(b).

As shown in Figure1(a), the absorption coefficient is relatively high at shorter wavelengths and decreases markedly as the wavelength increases. This spectral behavior is characteristic of crystalline silicon and agrees with the reference optical data reported by Green and Keevers, who tabulated the absorption coefficient, refractive index, and extinction coefficient of intrinsic crystalline silicon at 300 K over the wavelength range of 0.25–1.45 μm [17]. An updated self-consistent dataset reported by Green also confirms the strong wavelength dependence of the absorption coefficient of crystalline silicon over the same spectral range [1]. The decrease in the absorption coefficient toward longer wavelengths is associated with the reduction in photon energy and the approach toward the fundamental absorption-edge region of crystalline silicon, where optical absorption becomes considerably weaker [1,2,17]. The overlap of the calculated absorption spectra indicates that, within the assumptions of the present model, reducing the characteristic dimension over these regimes does not produce a distinguishable modification of the intrinsic absorption coefficient. As a result, even if the geometrical dimensions reach the nanoscale range, the computed absorption response is essentially bulk-like throughout this range. This distinction is crucial because the optical response does not necessarily have to be dominated by substantial quantum-confinement effects in order to achieve nanoscale dimensions. As silicon nanocrystals get closer to the characteristic confinement scale, their optical properties become more sensitive to quantum confinement; the most noticeable size-dependent changes often happen for nanocrystals that are only a few nanometers in size [6,9,18].

The (10–1) nm regime exhibits a fundamentally distinct behavior, as shown in Figure 1(b). The computed absorption spectra in this size range rely on particle size, and as the dimension decreases, the disparities between the curves become increasingly more noticeable. This behavior indicates that, within the present calculations, the absorption coefficient can no longer be represented by a single bulk-like spectrum as the silicon dimensions approach the few-nanometer scale. Experimental and theoretical investigations of silicon nanocrystals have demonstrated that spatial confinement of electrons and holes modifies the electronic states and produces size-dependent changes in the optical response [6,9,18]. The size dependence observed in Figure1(b) can be primarily associated with the quantum-confinement-induced modification of the effective energy gap. As the nanocrystal size decreases, stronger spatial confinement increases the separation between the relevant electronic energy states, resulting in an increase in the effective optical transition energy [6,9]. Consequently, the

absorption edge shifts toward higher photon energies, corresponding to shorter wavelengths. Such a size-dependent blue shift has been experimentally observed in silicon nanocrystals and represents one of the characteristic optical signatures of quantum confinement [6,18].

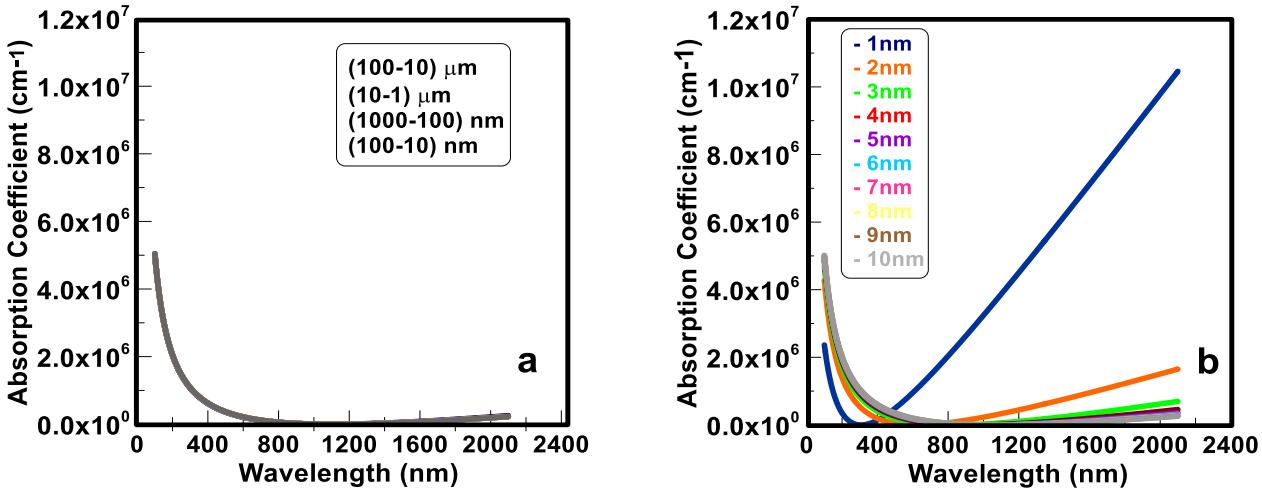

Figure 1 Calculated spectral absorption coefficient of crystalline silicon as a function of wavelength across different dimensional regimes: (a) bulk c-Si to the 100–10 nm regime, showing essentially bulk-like absorption behavior within the present model; and (b) Si quantum dots in the 10–1 nm regime, showing size-dependent absorption associated with quantum confinement.

The difference between Figure 1(a) and Figure 1(b) therefore, the comparison between Figure 1(a) and Figure 1(b) therefore reveals two distinct absorption behaviors within the present calculations. From (100–10) μm down to (100–10) nm, the absorption coefficient remains essentially unchanged with size and retains a bulk-like wavelength dependence. By contrast, in the (10–1) nm range, the absorption coefficient becomes increasingly size dependent because changes in the electronic structure can no longer be neglected. This transition is particularly important for the subsequent analysis of spectral transmittance, because changes in transmittance at larger dimensions may occur even while the intrinsic absorption spectrum remains unchanged, whereas in the few-nanometer regime the transmittance is influenced not only by the reduced dimension but also by the size-dependent modification of the absorption coefficient itself.

3.2. Theoretical spectral transmittance's size dependence

The computed spectral transmittance of crystalline silicon across the examined dimensional regimes is displayed in Figure 2, which gradually extends from the bulk range of (100–10) μm to the (10–1) nm range. As the effective optical path length decreases, the computed transmittance shows a systematic increase and broadening of the transmission spectrum. This behavior is related to the combined influence of the wavelength-dependent absorption coefficient and the propagation distance through the silicon structure. According to the Beer–Lambert relation, transmitted intensity decreases exponentially with the product of the absorption coefficient and optical path length; consequently,

reducing the propagation distance decreases optical attenuation and increases the transmitted fraction [19].

In the bulk regime (100–10) μm, as shown in Figure 2(a), the calculated transmittance remains relatively low over a substantial part of the investigated spectral range and becomes appreciable mainly toward longer wavelengths. This behavior follows directly from the relatively large optical path length together with the strong intrinsic absorption of crystalline silicon at shorter wavelengths. The optical constants reported for intrinsic crystalline silicon show that the absorption coefficient is high in the visible region and decreases strongly toward the near-infrared region [1,17]. Therefore, when the silicon thickness is relatively large, the product α L remains sufficiently high to suppress transmission over a broad wavelength range, even after the absorption coefficient begins to decrease. When the characteristic dimension decreases to (10–1) μm, the calculated transmission spectra (Figure 2 (b)) become broader and the transmittance increases relative to the bulk regime. Since the absorption-coefficient curves obtained in the present work remain unchanged between these two-dimensional regimes, this increase cannot be attributed to a modification of the intrinsic absorption spectrum. Instead, it results primarily from the reduction in the optical path length. A smaller value of L decreases the product α L, thereby allowing a larger fraction of the incident radiation to pass through the material at the same wavelength [19]. Thus, the comparison between the (100–10) μm and (10–1) μm regimes provides direct evidence, within the present model, that geometrical reduction alone can substantially modify spectral transmittance even when the absorption coefficient remains bulk-like.

A further decrease in dimension to the (1000–100) nm regime, as shown in Figure 2 (c), results in an additional increase in transmittance and a further broadening of the spectral region over which silicon becomes transmissive. In this regime, the calculated absorption coefficient still follows the same bulk-like spectral behavior; therefore, the observed increase in transmittance continues to be governed predominantly by the reduced optical thickness. Silicon structures with reduced optical path lengths can exhibit appreciable transmission even when the material retains a relatively high absorption coefficient [20]. Moreover, experimental optical studies of thin silicon films have shown that their transmission behavior is strongly affected by film thickness and optical constants [20,21]. When the silicon dimension is reduced further to the (100–10) nm regime, as shown in Figure 2 (d), the calculated transmittance becomes substantially higher over a broad wavelength interval. Within the present calculations, the absorption coefficient remains essentially unchanged from that of the larger-dimensional regimes. Consequently, the increase in transmittance in this size range should still be attributed mainly to the strong reduction in the propagation distance rather than to a major size-induced alteration of the absorption coefficient. This result is important because it demonstrates that entering the nanoscale range does not necessarily imply that quantum confinement is already the dominant mechanism controlling the optical response. Experimental studies of silicon nanocrystals indicate that pronounced quantum-confinement-induced changes in interband optical transitions become particularly evident when the nanocrystal diameter decreases to only a few nanometers [6].

Figure 2 (e) shows that the most distinct behavior is observed in the (10–1) nm regime. In contrast to the larger-dimensional ranges, the calculated transmittance in this regime is influenced not only by the extremely short optical path length but also by the size dependence of the absorption coefficient itself, as established in Figure 1(b). Therefore, the transmittance can no longer be interpreted purely as a geometrical thickness effect. At these dimensions, particularly toward the few-nanometer range, quantum confinement increasingly modifies the electronic states and effective transition energies [6,18].Experimental evidence from size-selected silicon nanocrystals has shown that reducing the nanocrystal size can shift the effective band gap toward higher energies, while spectroscopic studies

have demonstrated a simultaneous blue shift of the absorption edge and other optical-transition features for silicon nanocrystals with diameters below approximately 6 nm [18].

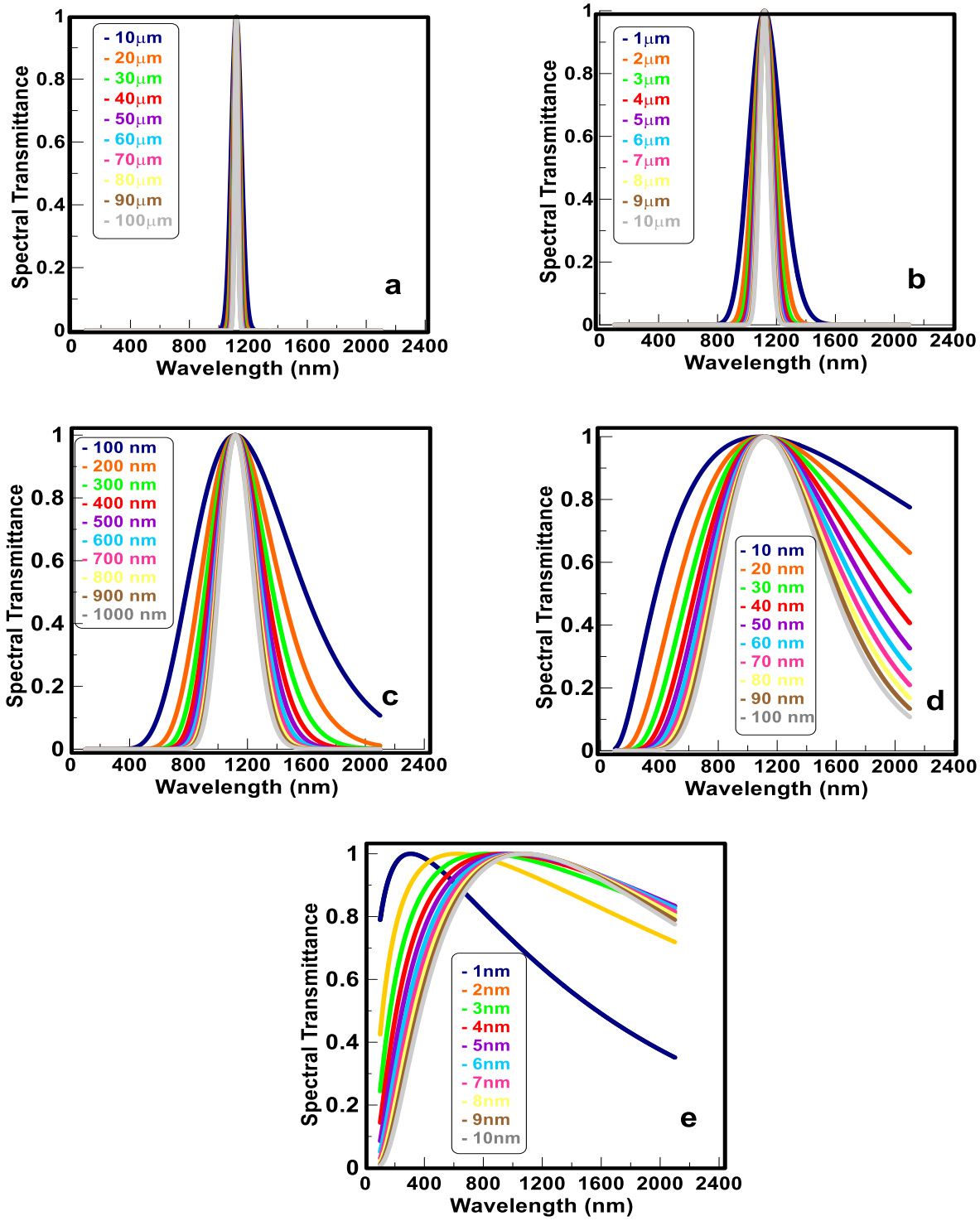

Figure 2 Calculated spectral transmittance of crystalline silicon as a function of wavelength across five dimensional regimes: (a) large-scale bulk c-Si (100–10) μm, (b) bulk c-Si (10–1) μm, (c) submicron Si (1000–100) nm, (d) silicon nanoparticles/nanocrystals (100–10) nm, and (e) silicon quantum dots (SiQDs) (10–1) nm.

Accordingly, the evolution of the calculated transmittance from the bulk to the few-nanometer regime can be separated into two principal mechanisms. For dimensions extending from (100–10) μm down to (100–10) nm, the calculated absorption coefficient remains essentially unchanged, and the systematic increase in transmittance is therefore dominated by the reduction in optical path length. By contrast, in the (10–1) nm regime, the dimension reduction is accompanied by a modification of the absorption spectrum itself. The transmittance in this range is consequently governed by both the reduced propagation distance and the size-dependent electronic structure associated with quantum confinement [6,18]. This distinction provides an important physical interpretation of the calculated spectra. The progressive increase in transmittance observed before the few-nanometer regime should not be interpreted as direct evidence of quantum confinement because it can be explained by the decrease in optical thickness while retaining a bulk-like absorption coefficient. Only as the characteristic dimension approaches the few-nanometer scale does the calculated optical response exhibit a simultaneous size dependence of both absorption and transmittance, consistent with the increasing influence of quantum confinement reported for silicon nanocrystals [6,18].

3.3 Comparison with experimental and reference data

In the large-scale bulk c-Si regime (10–100) μm, Figure 3(a), the experimental spectra of 30 and 75 μm crystalline Si samples show low transmittance in the visible region followed by a clear increase toward the near-infrared [22], consistent with the general spectral trend predicted by the present model. This behavior is associated with the strong decrease in the absorption coefficient of c-Si with increasing wavelength [1,17]. The higher transmittance of the 30 μm sample relative to the 75 μm sample also supports the expected influence of reduced optical path length on transmission. Differences in absolute transmittance values may arise, at least in part, from surface reflection and scattering, which are present in experimental structures but are not explicitly included in the simplified Beer–Lambert model [22]. For the bulk c-Si regime (1–10) μm, Figure3(b) compares the present calculation with the reference transmittance for a thickness of 5.5 μm derived from the experimentally reported absorption-coefficient data of Green and Keevers [17]. The reference spectrum exhibits the same progressive increase in transmittance toward longer wavelengths as the present calculations, indicating consistency with established c-Si absorption data. However, because the reference transmittance is itself derived from experimental absorption-coefficient data rather than obtained from an independent direct transmittance measurement, this comparison should be regarded as a reference-based consistency check rather than independent experimental validation.

In the submicron Si regime (100–1000 nm), Figure 3(c), the experimental spectrum of a 150 nm laser-crystallized Si film shows enhanced transmittance and a maximum in the near-infrared, in general agreement with the predicted increase in transmittance at reduced dimensions [23]. However, the experimental spectrum exhibits more pronounced spectral variations than the smoother behavior predicted by the present model. Multiple internal reflections, thin-film interference, grain boundaries, and microstructural effects—all of which are not specifically included in the simplified model—may be the cause of these discrepancies [2,23]. The current computations and the experimental spectra of a 50 nm annealed Si film are compared in Figure 3(d) for the 10–100 nm dimensional regime [24]. The experimental spectrum shows increasing transmittance from the ultraviolet toward the visible region but remains around 30–35% at longer visible wavelengths. Although the general increase in transmittance is consistent with the calculated trend, this comparison is based on a similar characteristic dimensional scale rather than an identical structural morphology. The size-dependent optical behavior observed in this regime is qualitatively consistent with the increasing influence of

quantum confinement predicted by the present model, since confinement modifies the electronic structure and shifts optical transitions as the nanocrystal size decreases [6]. However, the comparison should remain qualitative because the experimental Si nanocrystals are embedded in a SiO_x matrix and are additionally influenced by surface oxidation, interface states, and size distribution [25,26], effects that are not explicitly included in the present model.

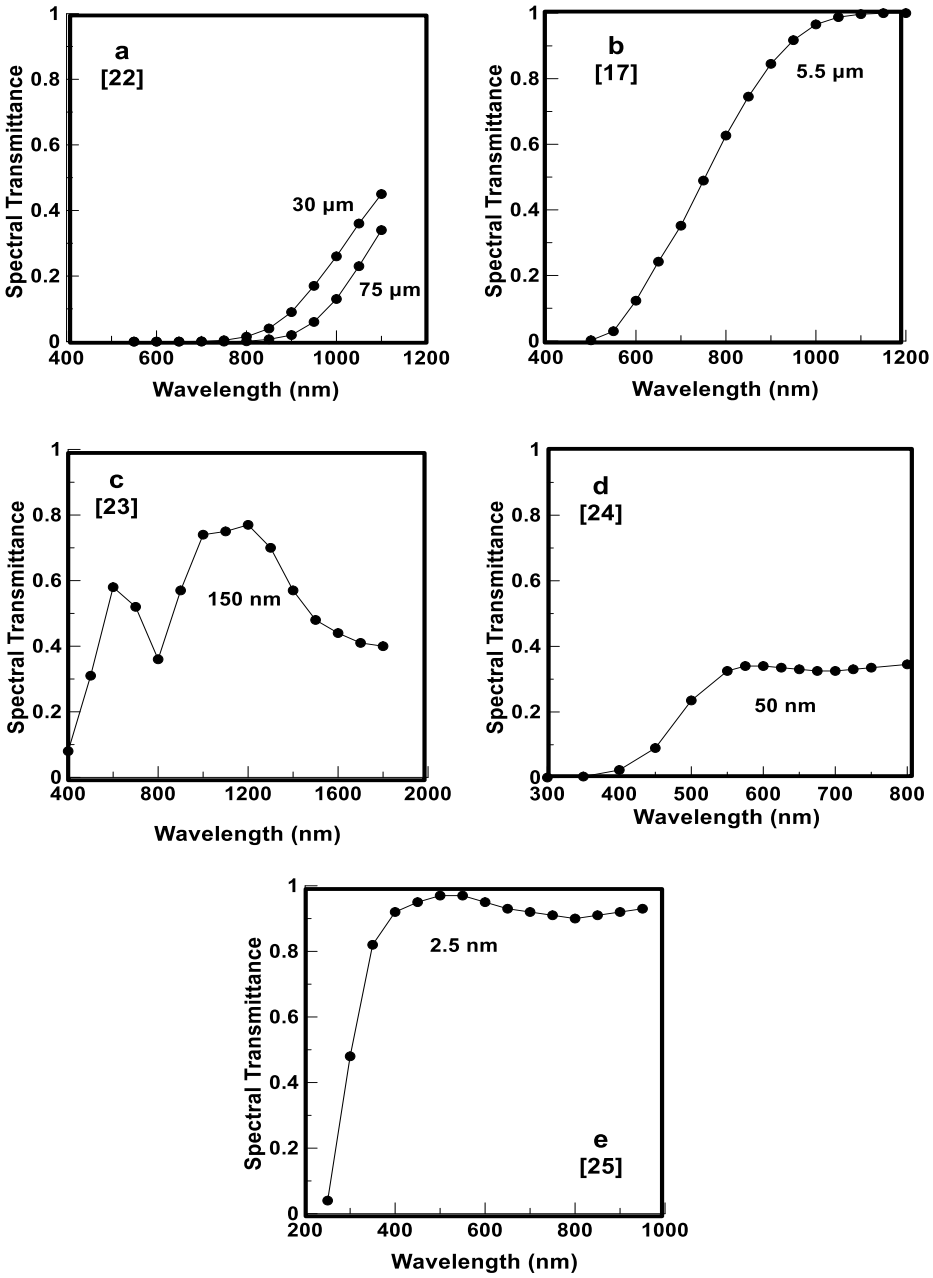

Figure 3 Comparison of the calculated spectral transmittance with experimental and reference-derived data across the five-dimensional regimes: (a) 30 and 75 μm crystalline Si samples [22]; (b) 5.5 μm c-Si, with reference transmittance derived from the experimental absorption-coefficient data of Green and Keevers [17]; (c) 150 nm Si film [23]; (d) 50 nm Si film [24]; and (e) Si nanocrystals with an average size of approximately 2.5 nm embedded in a SiO_x matrix [25].

Overall, the comparison shows good qualitative agreement between the calculated and experimental/reference spectral trends from the micrometer to the nanometer regimes. At larger dimensions, the calculated transmittance is governed primarily by the absorption coefficient and optical path length. At submicrometer dimensions, reflection, interference, interfaces, substrate effects, and microstructure can produce increasing deviations between the idealized calculation and experimental spectra. At dimensions of only a few nanometers, size-dependent electronic effects associated with quantum confinement become increasingly important, while surface and interface effects also contribute significantly to the experimentally observed optical response [6,25].

4. CONCLUSIONS

This study demonstrates a progressive evolution in the calculated optical response of crystalline silicon as its characteristic dimension decreases from the micrometer scale to the few-nanometer regime. From 100 μm down to tens of nanometers, the absorption coefficient remains essentially bulk-like within the present model, while spectral transmittance increases primarily because of the reduction in optical path length. Thus, enhanced transmittance in this dimensional range should not by itself be interpreted as evidence of quantum confinement. In (10–1) nm regime, the calculated absorption spectrum becomes increasingly size dependent as the effective band gap changes with decreasing SiQD size. Consequently, spectral transmittance in this regime is influenced by both the reduced propagation distance and the increasing contribution of quantum confinement to the electronic and optical response. Comparison with available experimental and reference-derived data shows good qualitative consistency in the overall spectral trends, while differences in absolute transmittance and spectral structure may be associated with effects not explicitly included in the simplified model, including reflection, interference, substrate, microstructural, and surface/interface effects. Overall, the results distinguish thickness-induced transmission enhancement from optical changes associated with quantum confinement and provide a continuous framework for describing the evolution of crystalline-silicon transmittance from bulk dimensions to the quantum-confined regime. This distinction may be useful for the dimensional design of silicon-based photonic and optoelectronic structures with tunable spectral responses.

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