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Photoluminescence study of hydrogen-passivated type-II silicon clathrate films

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While type-II silicon clathrates have shown promising room-temperature photoluminescence, their intrinsic optical properties remain unclear due to the presence of surface oxides, inhomogeneous and significant residual sodium concentrations, and contributions from disordered phases. These factors have hindered reliable identification of the emission band and limited development of the clathrates as light-emitting materials. In this work, we present a systematic photoluminescence (PL) study of deuterium-passivated, low-Na-doped, Si clathrate films, in which Na-related donor states and native defect levels are significantly reduced. A previously unrecognized emission feature associated with a surface oxide layer is identified and chemically removed, revealing a sharper emission spectrum composed of two dominant emission bands. We associate the higher energy band with the emission from the clathrate framework and the lower one with hydrogenated disordered or amorphous Si present as an impurity phase in the material. Temperature- and excitation-dependent PL measurements place the optical band gap of the clathrate phase near 1.9 eV, consistent with theoretical predictions. These results resolve long-standing ambiguities in Si clathrate PL emission and demonstrate a practical route to accessing near-intrinsic optical transitions. This lays the groundwork for engineering clathrate-based optoelectronic materials and highlights their potential as silicon-compatible light emitters.

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I. INTRODUCTION

Although diamond-structured silicon forms the foundation of modern semiconductor technology, its indirect band gap limits its efficiency as a light emitter, hindering its use in optoelectronic applications such as light-emitting diodes [1]. Consequently, extensive efforts have been devoted to identifying alternative Si-based materials that exhibit strong optical emission at room temperature. Nanocrystalline forms of Si, such as porous Si, have shown efficient, visible photoluminescence (PL), generally attributed to quantum confinement effects. However, their emission is highly dependent on surface passivation and tends to degrade upon oxidation [2,3]. Similarly, isolated Si quantum dots can exhibit high optical efficiency, which is strongly dependent on surface termination. For device applications there are additional challenges associated with contacting these quantum confined Si geometries. Hydrogenated amorphous silicon also exhibits broad room-temperature luminescence at around 1.3–1.4 eV but suffers from light-induced degradation [4]. Si-based superlattice structures, such as Si/SiO₂ multilayers and SiGe quantum wells or superlattices, emit light through confined carrier recombination, yet they are challenging to grow, and their performance is often limited by interface defects and low quantum efficiency [5–7]. In addition, SiGe alloys

with a hexagonal crystal structure were recently investigated as potential direct band-gap materials [8], but stabilizing this hexagonal phase remains synthetically challenging. Enhanced near-infrared emission has also been explored in Si doped with rare-earth ions, most notably erbium, where the luminescence arises from internal dopant transitions rather than the Si host; however, the efficiency remains limited and typically decreases significantly with increasing temperature [9,10]. More recently, type-II Si clathrate has garnered interest as an alternative to the above approaches with calculations predicting a direct or near-direct band gap and reports of room-temperature light emission in PL measurements [11–13]. As a bulk, crystalline Si compound (a Si allotrope) with fully tetrahedral bonding, type-II Si clathrate minimizes the surface-related issues of quantum-confined Si and the disorder effects of amorphous materials. It exhibits strong optical absorption and potential compatibility with existing Si device platforms.

Type-II Si clathrate consists of a framework of large and small cages, which are stabilized during synthesis by alkali metal guest atoms, typically sodium, that occupy interstitial sites within the cages [14]. With all cages filled, Na₂₄Si₁₃₆ is formed. However, Na_xSi₁₃₆ (0 < x < 24) can be formed by controlling Na activity during synthesis along with post-growth chemical treatments and diffusion processes. With these approaches, Na concentrations have been lowered to approximately 10¹⁸ cm⁻³, a level at which the clathrate exhibits characteristics of a heavily doped semiconductor with Na acting as a donor atom [11,15]. A broad PL peak in the range of 1.65–1.7 eV has been associated with emission from the type-II clathrate phase [11–13,16]. The peak position

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has been reported to shift with Na concentration and is also influenced by defects [12,13]. The recombination mechanism giving rise to the peak (e.g., defect-related emission, donor-acceptor recombination, or emission from disordered states) is not well understood, making band-gap determinations based on the peak position difficult. While the PL peak energy is consistent with band-gap values inferred from absorption measurements, it is below the predicted theoretical value of 1.9–2.0 eV [17,18].

Recent work by our group demonstrated that hydrogen plasma treatment effectively passivates the clathrate, reducing both Na doping levels and native defect densities and resulting in enhanced PL intensity and a blueshifted emission peak near 1.76 eV [19]. We attributed this to suppression of sub-band-gap recombination [19]. In this work, we explore in more detail the clathrate PL spectrum using temperature- and excitation-energy-dependent measurements of thin-film samples with and without H plasma passivation treatment. We find that surface oxide phases contribute features to the PL spectrum. Oxide etches are shown to minimize this contribution. We also associate a luminescence peak near 930 nm with hydrogenated disordered or amorphous material. Focusing on the PL band peaked near 700 nm that was previously associated with the clathrate, our measurements support this identification and lead to the conclusion that the near-intrinsic band gap of type-II Si clathrate is close to 1.9 eV, in agreement with theoretical predictions. Most notably, we successfully isolated a near-intrinsic emission spectrum from the clathrate phase itself. These results resolve long-standing ambiguities in the interpretation of Si clathrate PL spectra and establish type-II Si clathrate as a promising material for next-generation Si-based light-emitting applications, with potential for direct band-gap-like behavior.

II. EXPERIMENTAL METHODS

Type-II $\text{Na}_x\text{Si}_{136}$ clathrate films were synthesized following a procedure adapted from Refs. [11,20], with full details provided in the Supplemental Material [21]. After synthesis, the films were treated with a deuterium plasma using a custom-built inductively coupled plasma system, as discussed in Ref. [19] and described in more detail in the Supplemental Material [21]. Based on prior electron paramagnetic resonance (EPR) measurements [19], the plasma treatment passivates most of the Na in the film, resulting in Si clathrate films containing active Na donors at concentrations on the order of 10^{17} cm^{-3} . This places the material in the semiconducting regime. PL spectra were acquired using an Acton 300i spectrometer equipped with a 150 g/mm grating and a 100 μm entrance slit. The detector was a Princeton Instruments Spec-10:100BR silicon charged-coupled device detector array, cooled by liquid nitrogen. Excitation lasers of 460, 550, and 660 nm were used. To block scattered laser light from entering the spectrometer, a 550 nm long-pass filter was used for 460 and 532 nm excitation, while a 675 nm long-pass filter was used for 660 nm excitation. All spectra were collected with a 10 s integration time and were background corrected by subtracting a dark spectrum acquired under identical conditions.

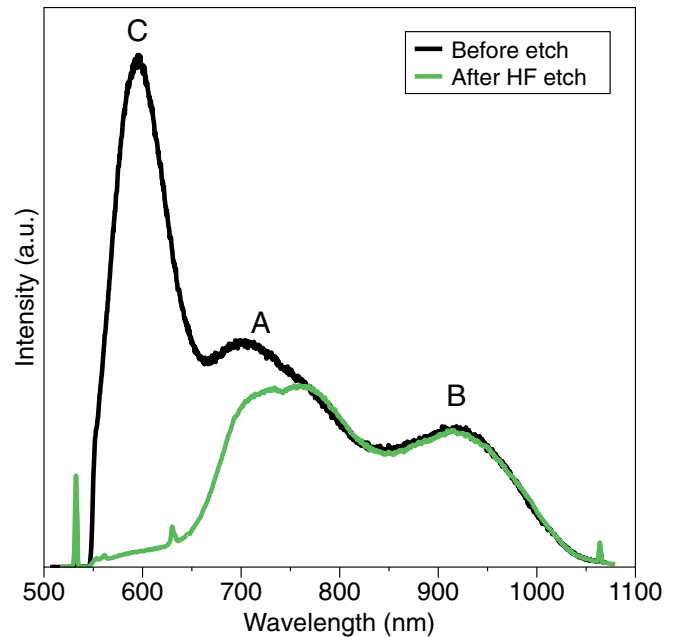


FIG. 1. Room-temperature photoluminescence (PL) spectra of the hydrogen-passivated Si clathrate film before (black curve) and after (green curve) HF etching. The film was passivated at 200 °C with 100 W RF power for 1.5 h at a pressure of 150 mTorr. The green curve corresponds to a sample etched in a 5 vol % HF solution for 2 min and was scaled to match the intensities of peaks A and B for comparison. The excitation wavelength was 532 nm. Sharp features at 532 and 1064 nm originate from the laser, while other minor peaks arise from filter artifacts.

III. RESULTS AND DISCUSSION

Our previous work showed that hydrogen (deuterium) passivation significantly enhances the PL emission intensity of Si clathrate films and shifts the emission peak to lower wavelengths, likely by suppressing sub-band-gap recombination [19]. However, we often observed a PL feature near 600 nm on the short-wavelength edge of the spectrum which varied in intensity from sample to sample and from location to location on the same sample. Given the high energy and lack of reproducibility, we concluded it was unlikely to arise from the clathrate [11]. The black curve in Fig. 1 shows a PL spectrum from a passivated type-II Si clathrate film under 532 nm excitation, where three peaks are present. A three-Gaussian fit of the same spectrum (Fig. S1) resolves these components [21]. Previously, we used Raman scattering in conjunction with PL to show that peak A appears in regions exhibiting the clathrate Raman signature, confirming its origin in the clathrate phase [11]; subsequent reports by other groups reached the same conclusion [12,13]. Peak B is attributed to an impurity phase, as discussed in Ref. [19] and below. In contrast, peak C is the 600 nm feature. It disappears after a short HF etch (see green curve in Fig. 1), supporting our conclusion that it is not related to the clathrate and originates from a surface oxide. This oxide is unlikely to be SiO_2 , which commonly forms on Si surfaces and has been observed in the PL from porous Si with a large surface area [3]. Instead, it is probably a Na-containing species, such as sodium silicate,

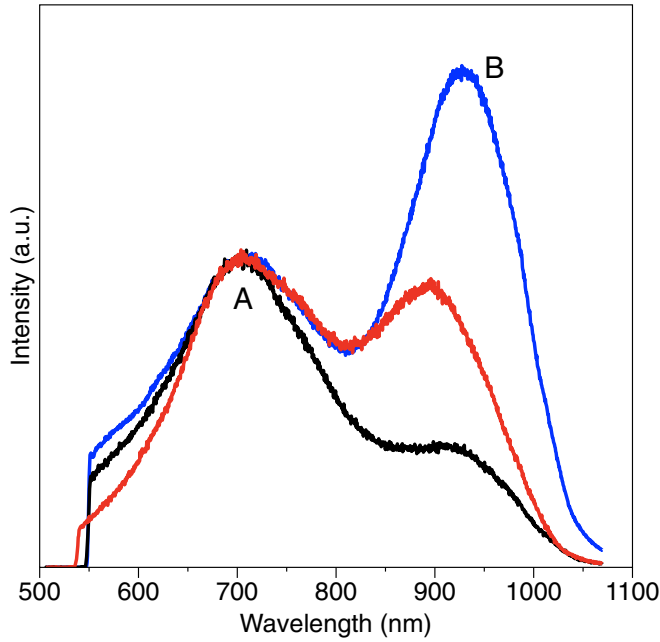


FIG. 2. Room-temperature PL spectra of hydrogen-passivated Si clathrate films under 460 nm laser excitation. The black, red, and blue curves correspond to samples passivated at 200 °C with 100 W RF power, 250 °C with 150 W RF power, and 300 °C with 200 W RF power, respectively. All treatments were performed for 1.5 h at a pressure of 150 mTorr. Peaks A and B correspond to distinct emission features. We note that the shape of peak B beyond 1000 nm is affected by the drop in sensitivity of the detector.

formed during synthesis. Supporting this idea, we find that peak C does not return even after a month of air exposure in a humid environment. In addition, Tamin et al. recently reported x-ray photoelectron spectroscopy and Auger spectra of type-II Si clathrate films consistent with the presence of a Na-containing oxide on the surface [22]. In the following discussion, the samples have all been subjected to an HF etch to minimize or remove peak C.

Figure 2 explores how the PL emission of Si clathrate films responds to different plasma treatment conditions. The spectra were obtained under 460 nm laser excitation from three samples treated with varying plasma powers and sample temperatures while keeping the pressure and treatment duration constant. From Fig. 2 we see peak B becomes more pronounced with higher temperature and plasma power, likely due to increased deuterium incorporation. Across all three samples, the main clathrate peak (peak A) consistently shifts to shorter wavelengths, from approximately 760 nm before treatment to around 700 nm after, in agreement with our previous studies [19]. An additional contribution at the lower-wavelength end is also observed as an inflection in the slope. We attribute it to the same surface oxide as discussed above.

To further investigate the distinct emission mechanisms underlying peaks A and B, we performed temperature-dependent PL measurements (Fig. 3) under 460 nm excitation from 10 K to room temperature on the sample corresponding to the black curve in Fig. 2. Both peaks exhibit increased intensity as the temperature decreases, while a weak contribution from peak C is consistently observed. To separate the overlapping

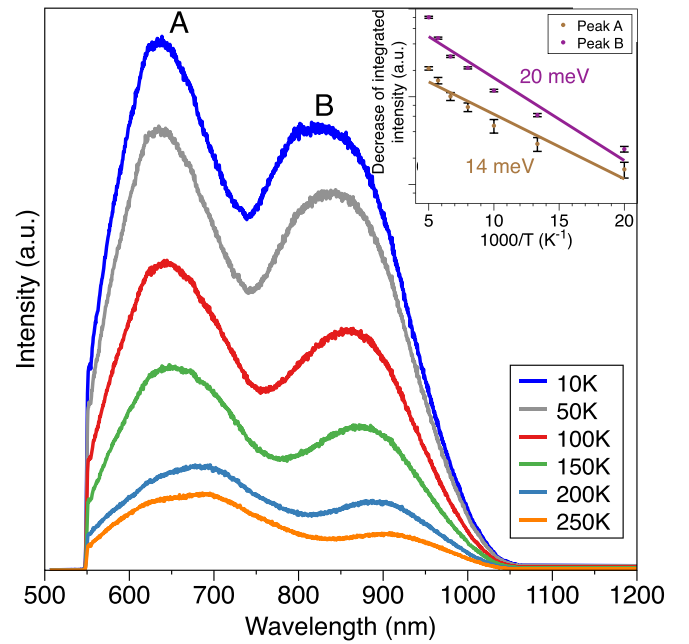


FIG. 3. Temperature-dependent PL spectra of the deuterium-passivated Si clathrate film (same sample as the black curve in Fig. 2), measured from 250 to 10 K under 460 nm laser excitation. The inset shows the Arrhenius plots used to extract the activation energies for peaks A and B. Error bars represent the 95% confidence intervals derived from the Gaussian fitting parameters. The inset (log scale) shows the extracted activation energies for the two peaks based on temperature-dependent PL measurements of the sample represented by the black curve.

features, a three-Gaussian fitting approach was used. We first determined the center and width of peak C from the fit (Fig. S1 [21]) of the pre-etch PL spectrum measured under 532 nm excitation, where the oxide feature (peak C) is more pronounced, and used these values as fixed parameters in the fitting [21]. Only the intensity of peak C was allowed to vary. Figure S2 presents a representative fit for the spectrum measured at 200 K, and similar fittings were performed at other temperatures [21]. The integrated areas I of the fitted Gaussian components associated with peaks A and B were then used to quantify their intensity variations with temperature.

Activation energies were extracted by plotting the decrease in integrated PL intensity relative to the 10 K intensity, defined as $(I_{10K} - I_T)/I_T$, as a function of inverse temperature. The resulting Arrhenius plots are shown in the inset of Fig. 3. Peak A displays an activation energy of approximately 14 meV, consistent with our previous PL results from the buried interface of Si clathrate films [11]. This value also closely aligns with the temperature dependence of the Na-related hyperfine intensities observed in EPR measurements of Si clathrate powders [23]. This consistency in activation energy for samples with nearly an order of magnitude lower donor concentration than in our previous study supports the conclusion that Na acts as a shallow donor in type-II Si clathrates.

In contrast, peak B exhibits a larger slope in the Arrhenius plot (inset of Fig. 3), suggesting more deeply localized radiative centers than those associated with peak A. Interestingly, the activation energy (20 meV) of peak B falls within

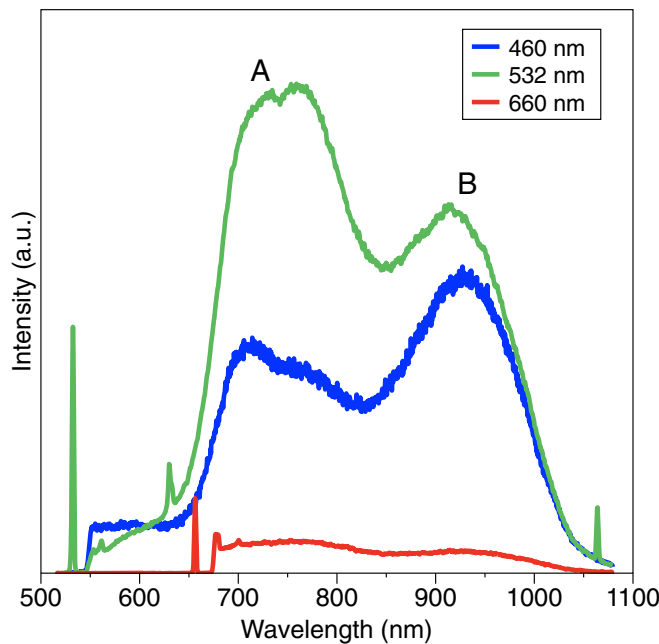


FIG. 4. PL spectra for the passivated and etched Si clathrate film (200 °C, 100 W, 1.5 h, 150 mTorr) under different laser excitations. The film was etched in 5 vol % HF for 2 min. On the red curve, the sharp line at 660 nm is a residue of the excitation laser line, and the oscillations around 700 nm are from interference in the long-pass filter. On the green curve, the sharp lines at 532 and 1064 nm are due to the laser; other small, sharp structures come from the long-pass filter. The flat region below 650 nm on the blue curve and the similar sloped region on the green curve are attributed to a small residue of peak C and background luminescence arising from scattered laser light. All spectra are normalized by laser power.

the range reported for shallow-level thermal quenching in hydrogenated amorphous Si-based materials [24–26], indicating the recombination process giving rise to peak B is distinct from that of peak A. We previously showed from x-ray diffraction (XRD), Raman scattering, and EPR measurements that disordered or amorphous Si is a common impurity phase produced as a by-product of type-II clathrate synthesis [11,15], located on the film's top surface and along the grain boundaries. We have developed various etching treatments to minimize the amount of disordered Si but always find some is present in the material [11]. The hydrogen plasma treatment likely enhances luminescence by passivating dangling bonds in this disordered phase, thereby suppressing nonradiative recombination and enabling radiative recombination through localized states within the band gap of amorphous Si. In fact, peak B is not new. In films not subjected to an acid etch or plasma treatment, a broad emission band around 930 nm was previously observed and attributed to surface inhomogeneities [11]. The present evidence suggests that peak B has a different origin than peak A, as discussed in more detail below. A better understanding of peaks A and B, along with the identification and removal of peak C, enables more detailed excitation-dependent studies to probe the intrinsic emission behavior of Si clathrate, which will be discussed next.

Figure 4 compares the PL spectra of a passivated and HF-etched Si clathrate film under different excitation wavelengths. All three spectra exhibit peaks A and B; however, the overall PL intensity under 660 nm excitation is significantly lower, suggesting that the 1.88 eV photon energy is near the band gap of the type-II Si clathrate film. Notably, peak A appears to consist of two closely overlapping components, observed under both 460 and 532 nm excitation. This feature consistently appears across multiple samples treated under varying plasma conditions. One possible explanation is that surface structures formed during HF etching (2 min in a 5 vol % solution) introduce additional radiative states, as this feature is not observed after treatment with either more dilute HF (1–3 vol %) or shorter etch durations (~ 10 s), suggesting that its origin may be associated with the more aggressive HF etching conditions. Alternatively, this feature may be intrinsic to the band structure of type-II Si clathrate, as theoretical calculations predict a direct band gap closely accompanied by a nearby indirect transition [27]. Because these two transitions are so close in energy, they cannot be reliably separated with the current data. The main objective of this analysis is to distinguish the emission from the clathrate framework from that of other phases such as surface oxide and disordered silicon. Since both overlapping components of peak A are attributed to the clathrate phase, summing them provides a reasonable first-order approximation of the total clathrate-related emission intensity shown in the inset of Fig. 3. Further investigation is needed to determine the precise origin of the substructure within peak A.

The choice of 660 nm for one of the laser wavelengths was fortuitous and provides additional confirmation of a band gap near 1.9 eV. Figure 5(a) shows the PL spectra of the passivated and HF-etched Si clathrate film (same sample as in Fig. 4) measured at various temperatures under 660 nm laser excitation. The inset displays the room-temperature spectrum from the same sample and location, again with peaks A and B both visible. As the temperature decreases, peak B grows while peak A gradually diminishes. It becomes undetectable below approximately 200 K. The disappearance of peak A at lower temperatures indicates that the absorption edge and band gap of the Si clathrate shifted to higher energy than those of the excitation source as temperature decreased. This behavior is consistent with Fig. 3, which shows temperature-dependent PL spectra measured with 460 nm excitation. Here the center of peak A shifts from around 700 nm at room temperature to approximately 630 nm at 10 K, consistent with a temperature-dependent change in the band gap. At low temperatures, the 660 nm excitation is no longer sufficient to excite clathrate emission due to the widened band gap, resulting in the loss of peak A. This further supports a band gap near 1.9 eV, with the 1.88 eV excitation energy slightly below the band gap at low temperature. However, the fact that the 660 nm excitation is still able to excite peak B is evidence that B arises from a different source.

We can, in fact, use the temperature-dependent results in Fig. 5(a) to isolate peak A. In Fig. 5(b), the scaled and energy-aligned PL spectrum acquired at 150 K under 660 nm excitation is first subtracted from the room-temperature spectrum of the same sample measured under 532 nm excitation, removing the contribution from peak B (gray curve).

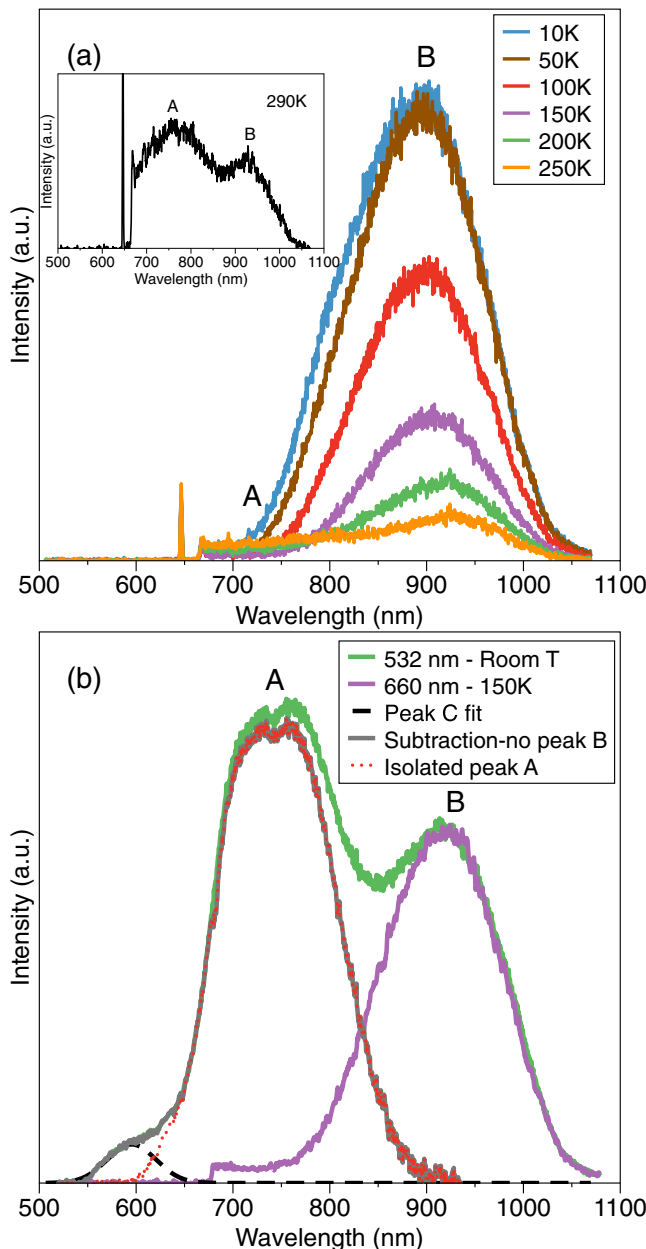


FIG. 5. (a) PL spectra of the passivated and etched Si clathrate film (same sample as in Fig. 4) measured at different temperatures under 660 nm laser excitation. The inset shows the emission from the same sample and location at room temperature. (b) Isolation of the clathrate-related PL emission under 532 nm excitation. The green curve shows the room-temperature PL spectrum under 532 nm excitation reproduced from Fig. 4 (sharp features from the laser and filter have been removed). The purple curve represents the scaled and energy-aligned 660 nm, 150 K PL spectrum corresponding to the peak B contribution. The oxide-related peak C fit is shown as a dashed black curve. The gray curve results from subtracting the peak B contribution from the 532 nm PL emission, and the red dotted curve is obtained by further removing the peak C fit from the gray curve, yielding the isolated clathrate-related PL emission.

However, a small residual oxide-related feature remains near 600 nm. To remove this contribution, we further subtracted the scaled peak C fit obtained from the three-Gaussian analysis

of the pre-etch data (Fig. S1) [21]. The resulting red dotted curve in Fig. 5(b) represents the isolated clathrate-related emission, which can be considered a close approximation to near-intrinsic emission from the type-II Si clathrate film. The resulting spectrum exhibits well-defined high- and low-energy edges, consistent with emission from a material with low doping and defect density. Similar analyses were performed for the room-temperature PL spectra obtained under 460 and 660 nm excitation. For the 460 nm excitation, the background arising from scattered excitation laser light was first removed, followed by subtraction of the oxide-related feature and peak C contributions (Fig. S3) [21]. For the 660 nm excitation, no oxide feature was detected, and only the peak B component was subtracted (Fig. S4) [21]. A more detailed discussion of the procedures for isolating peak A under 460 and 660 nm excitation, as well as for determining the error bars of their integrated intensities, is given in the Supplemental Material [21].

Identifying and removing peak C revealed a much sharper short-wavelength edge on peak A. This, along with the temperature-dependent variation of the PL spectra under 660 nm excitation, enables an effective isolation of peak A and a more precise estimate of the band gap of type-II Si clathrate. In Fig. 6, the black dots represent the integrated intensity of peak A at the three different excitation wavelengths. They represent three points of the PL excitation spectrum (PLE) for peak A. Although this is not a full PLE curve, which typically involves continuous tuning of the excitation wavelength, it is sufficient to define the overall shape of the curve and to narrow the band-gap energy. The isolated clathrate related PL emission spectra (peak A) excited at 460 and 532 nm, are also included for reference. The intersection points between the low-energy side of the “excitation spectrum” and the high-energy edge of the PL emission spectra occur near 1.91–1.93 eV. This energy marks the onset of excitation, where the photon energy becomes sufficient to generate radiative transitions. This crossover point identifies the optical band gap of type-II Si clathrate in samples that, owing to their low Na content and effective passivation, are closer to intrinsic than those used in previous studies. Although we and others previously reported an absorption band gap near 1.7 eV, we believe the 1.91–1.93 eV value obtained here is closer to the intrinsic band gap. We suspect that sub-band-gap absorption, either from the amorphous impurity phase or from defect states, is responsible for absorption below the intrinsic band gap of the type-II material.

It is interesting to see the reduction in peak A intensity under 460 nm excitation compared with 532 nm. To verify that this decrease was not an artifact of measurement geometry, such as a difference in laser spot size or variation in collection geometry, we tested a GaAs quantum well reference sample. In that case, the integrated PL signal increased monotonically with decreasing excitation wavelength, consistent with expectations. This confirms that the suppression of peak A at 460 nm is a property of the clathrate sample. This can be explained by differences in laser penetration depth: 460 nm excitation is absorbed closer to the surface, enhancing surface-related contributions, whereas 532 nm penetrates more deeply, probing bulk clathrate states. The weaker relative intensity of peak A under 460 nm excitation may also reflect enhanced

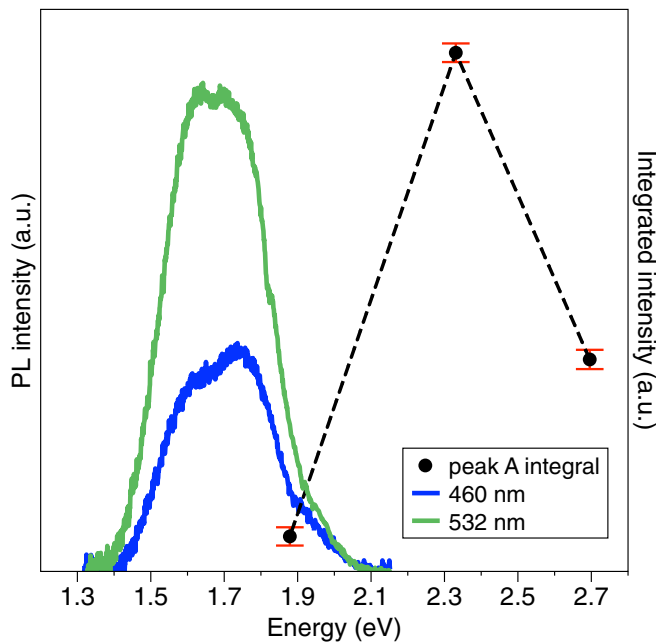


FIG. 6. Overlay of isolated clathrate-related PL emission spectra (with sharp laser filter related lines removed) under 460 and 532 nm excitation, along with the integrated intensity of peak A under all three excitation energies. The integral of peak A is plotted as black dots at each excitation wavelength, and the dotted line serves as a guide to illustrate the trend in the peak A intensity as a function of excitation energy. Error bars were estimated separately for each excitation wavelength based on the dominant sources of uncertainty: for 460 nm excitation, from variations before and after sequential subtraction of the peak B contribution, the scattering component, and residual oxide emission; for 532 nm excitation, from differences before and after oxide subtraction [gray and red curves in Fig. 5(b)]; and for 660 nm excitation, from a comparison of the integrated intensity from the Gaussian fit with twice the area of the right half of the truncated peak A. Further details about the peak A isolation (460 nm) and error-bar determination are provided in the Supplemental Material [21].

surface recombination and a higher defect density near the surface, in contrast to the buried clathrate layer, which generally exhibits better optical quality [11]. This is clear in Fig. S5, where the relative integrated intensity of peak A to peak B decreases with increasing excitation energy [21]. This suggests peak B is less affected by surface effects and, again, supports the conclusion that the two peaks originate from distinct phases or emission centers.

Based on these observations, we attribute peak B to hydrogenated amorphous or disordered Si. Several findings support

this assignment: the increase in peak B intensity after hydrogen plasma treatment, which passivates dangling bonds and may create new luminescent centers; its higher activation energy (inset in Fig. 3) and distinct temperature dependence compared with peak A; its persistence under sub-band-gap excitation, when peak A disappears; and its relative enhancement at higher excitation energy, where surface recombination plays a large role. The emission energy of peak B, along with these features, agrees well with previously reported luminescence from hydrogenated amorphous Si [24–26]. Moreover, XRD, Raman, and EPR measurements confirm the presence of disordered Si in our samples [11,15], which cannot be fully eliminated even after repeated etching treatments. While we cannot rule out the possibility that peak B originates from defect states within the clathrate itself, this distinction does not alter the key conclusion that peak A arises from the intrinsic clathrate framework.

IV. CONCLUSIONS

In this work, we systematically investigated the PL properties of type-II silicon clathrate films approaching intrinsic behavior. By identifying and removing a previously unrecognized emission feature originating from a surface oxide layer, we were able to resolve a sharper and more defined clathrate PL spectrum. Temperature-dependent and excitation-wavelength-dependent PL measurements revealed that the two dominant emission peaks arise from distinct phases: the Si clathrate framework and hydrogenated amorphous Si. These measurements also allowed us to estimate the near-intrinsic band gap of type-II Si clathrate to be approximately 1.9 eV, consistent with theoretical predictions for a direct gap transition in this structure. Taken together, these findings resolve long-standing ambiguities in the PL behavior of Si clathrate materials and provide direct experimental evidence supporting their classification as potential direct band-gap semiconductors. This work also advances the fundamental understanding of emission mechanisms in alternative Si allotropes and highlights type-II Si clathrate as a promising candidate for next-generation light-emitting materials.

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DATA AVAILABILITY

The data that support the findings in this manuscript are available from the authors upon reasonable request.

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