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Hydrogen-related 3.8 eV UV luminescence in α-Ga_2O_3

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ABSTRACT

Temperature-dependent photoluminescence was used to investigate the impact of H on the optical properties of α-Ga_2O_3 films grown by halide vapor phase epitaxy. An additional UV luminescence line centered at 3.8 eV is observed at low temperatures, which strongly correlates with the concentration of H in the films. This luminescence line is assigned to donor–acceptor pair recombination involving an H-related shallow donor and H-decorated Ga vacancy (V_{Ga}-nH) as the acceptor, where n = 1, 2, 3. Previous reports have already suggested the impact of H on the electrical properties of Ga_2O_3, and the present study shows its clear impact on the optical properties of α-Ga_2O_3.

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Gallium oxide (Ga_2O_3) is an emerging wide bandgap semiconductor with promising applications in power electronics and solar-blind photodetectors.[1] Ga_2O_3 is a polymorphic compound, with known phases labeled as α, β, δ, γ, and κ. Much attention has been dedicated to the thermodynamically stable monoclinic β-phase. However, the rhombohedral α-phase of Ga_2O_3 exhibits many advantages over the other phases of Ga_2O_3. Notably, it exhibits the highest bandgap (*ca* 5.1–5.3 eV) among all phases,[2–5] which should result in a higher breakdown electric field value of 9.5 MV/cm compared to 8 MV/cm for β-Ga_2O_3,[6,7] and offers interesting prospects for bandgap engineering through alloying with several isomorphic sesquioxides, such as Al_2O_3,[8] In_2O_3,[9] Fe_2O_3,[10] or Ti_2O_3.[11] Thus far, most of the attention of α-Ga_2O_3 research has been focused on material growth, leaving a gap in the knowledge of the properties of defects in the material. However, to improve the efficiency and reliability of Ga_2O_3-based devices, it is crucial to understand the influence of defects on the electrical and optical properties of α-Ga_2O_3.

Photoluminescence (PL) is a well-established method for investigating the influence of defects on the optical properties of semiconductors.[12] PL studies on α-Ga_2O_3 remain relatively scarce compared to the other polymorphs. While this comes perhaps as a surprising result owing to the different crystal structures, several studies have reported no notable difference in the luminescence properties of α- and β-Ga_2O_3.[13–15] Furthermore, deep level transient and optical deep level transient spectroscopy studies of α-Ga_2O_3 and β-Ga_2O_3 also showed the two polymorphs exhibited a similar distribution of defect energy levels within the bandgap.[16] Therefore, it seems reasonable in the first instance to refer to literature on PL of β-Ga_2O_3 to initiate a review on luminescence of α-Ga_2O_3.

Typically, β-Ga_2O_3 exhibits luminescence in the UV (3.2–3.6 eV),[17–19] blue (2.8–3.0 eV),[17,20] and green (2.5 eV)[21] spectral regions, with luminescence in the red (1.7–1.9 eV) also reported.[22–24] Two UV lines have been assigned to intrinsic origins, with experimental and theoretical calculations attributing the luminescence to the recombination of free electrons with self-trapped holes (STHs).[18,25] However, Onuma *et al.* suggested that the UV luminescence was composed of not only the recombination of STH and free electrons but also had a contribution from donor–acceptor pair (DAP) recombination involving Si as a shallow donor with potential acceptors being Ga vacancies (V_{Ga}), substitutional Mg (Mg_{Ga}), substitutional N (N_O), and O–Ga divacancies (V_O–V_{Ga}).[17] The blue luminescence is typically associated with DAP recombination involving a host of intrinsic defects with V_O, V_{Ga}, V_O–V_{Ga}, Mg_{Ga}, and Ga interstitials (Ga_i) suggested as possible donors and acceptors.[26,27] The green luminescence line is less studied with attribution thus far being to DAP recombination involving a range of defects including O_i and V_{Ga}.[19,22] Finally, red

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luminescence has been linked to H or N impurities[23,28] as well as reported sharp red luminescence lines attributed to the incorporation of Cr^{3+} ions.[24]

H is a common yet elusive impurity in Ga_2O_3, and the scarce reports have shown it can have dramatic impact on the properties of the material, such as controlling n- and p-type conductivity in β-Ga_2O_3,[29] as well as having an adverse effect on photocurrent.[30] H is predicted to act as a shallow donor, occupying either interstitial (H_i) or substitutional sites (H_O), and the low formation energy in both configurations suggests that it will be easily incorporated into the crystal lattice.[31,32] Furthermore, the low migration barrier means we can expect H to diffuse in the lattice and interact with other defects such as V_{Ga}, where the vacancy has four dangling bonds that can readily accept the H and form complex V_{Ga}-nH defects, where n is the number of H atoms in the complex.[31] Theory predicts that formation of V_{Ga}-nH complexes in β-Ga_2O_3 is indeed more energetically favorable than that of the isolated V_{Ga}.[33] The state of the art suggests that H in V_{Ga}-nH is strongly bound, so much so that work from Wei *et al.* calculated theoretically that temperatures in excess of 1000 K are required to dissociate the complex.[34] The influence of V_{Ga}-nH on the electrical properties of Ga_2O_3 has been studied by Islam *et al.* who demonstrated that by controlling the H incorporation in the crystal, the conductivity of the material was switched from n-type (when $n = 4$) to p-type ($n = 1, 2, 3$).[29]

As the impact of H on the electrical properties has become more established, there is a gap in the literature regarding the impact of H on the luminescence properties of the material. Jiang *et al.* studied the effect of H_2 plasma treatment on the electrical and optical properties of β-Ga_2O_3 films and observed a decrease in the luminescence of samples exposed to H_2 plasma.[35] Huynh *et al.* investigated H-doped β-Ga_2O_3 films by cathodoluminescence and reported the emergence of a red luminescence band centered at 1.9 eV after the film was exposed to H_2 plasma treatment.[23] In the present paper, we employ temperature-dependent PL to study the optical properties of α-Ga_2O_3 films grown by halide vapor phase epitaxy (HVPE) containing variations of H and Cl concentrations, where the variation stems from a variation in gas partial pressures of $GaCl_x$ and H_2 used during the growth process to stimulate rapid growth.

The α-Ga_2O_3 films were grown on *c*-plane sapphire by halide vapor phase epitaxy in a lab-made quartz reactor at 520 °C under atmospheric pressure. O_2 (>99.999 95% pure) and GaCl were used as the precursors. The GaCl was synthesized by a chemical reaction of metal Ga (>99.999 99% pure) and HCl gas (>99.999% pure) upstream in the reactor at 570 °C. Additional HCl gas was also supplied to enable rapid growth.[36] N_2 (dew point <−110 °C) was used as the carrier gas. The growth conditions are summarized in Table I, with P_0(X) being the supply partial pressure of gas X. The films were grown in two steps except for sample A. Samples B–D were grown relatively slowly at the first step, and the growth rate was increased at the second step by increasing the partial pressure of $GaCl_x$ and H_2 where H_2 was produced by the chemical reaction of Ga and HCl in the reactor yielding different concentrations of H and Cl, as measured by secondary ion mass spectrometry (SIMS) as reported in Table I. Here, we note that C, N, Si, and S levels were measured but the concentrations were below the SIMS detection limit. All the films had a thickness in the range 3.5–3.8 μm. The samples were also analyzed by x-ray diffraction (XRD), showing excellent phases purity (Fig. 1S), and the broadening of the symmetric and asymmetric reflections is reported in Table I.

TABLE I. Summary of the growth conditions and impurity concentration for the sample set.

Sample	A	B	C	D
P_0 (GaCl) (kPa)	0.125	0.125/0.25	0.125/0.5	0.125/1.0
P_0 (H_2) (kPa)	0.063	0.063/0.125	0.063/0.25	0.063/0.5
P_0 (O_2) (kPa)	1.25		1.25/3.125	
P_0 (HCl) (kPa)	0.125		0.125/1.25	
Growth rate (μm/h)	11.9	11.9/34.1	11.9/73.4	11.9/116
Thickness (μm)	3.8	0.4/3.4	0.4/3.2	0.4/3.1
[H] (cm^{-3})	$<6 \times 10^{16}$	1.1×10^{17}	1.5×10^{17}	2.8×10^{17}
[Cl] (cm^{-3})	1×10^{16}	1.8×10^{17}	4.1×10^{17}	1.4×10^{18}
Tilt 0006 (arc sec)	⋯	135	359	103
Twist 10-12 (arc sec)	⋯	1820	1442	1361

The optical properties of the films were evaluated using temperature-dependent PL measurements between 9 and 290 K. A Photon Systems 224 nm HeAg pulsed laser was used as an excitation source. The luminescence from the samples was collected by a McPherson 207 monochromator with a 300 line mm^{-1} diffraction grating, and the light was detected by an Andor Technology CCD camera cooled to −50 °C. A 280 nm low-pass filter was positioned at the entrance of the spectrometer to remove the laser lines from the collected signal. This filter was replaced by a 470 nm low-pass filter to assess the presence of second order diffraction of the signal.

Figure 1(a) shows the typical 290 K spectrum of sample C. The PL spectra exhibit broad emission bands centered at 3.3 eV (UV), 2.7 eV (blue), and 1.6 eV (red) in close agreement with the literature.[17,18,24] Furthermore, we can distinguish an additional low intensity luminescence centered at 3.8 eV in the spectra in log scale [inset Fig. 1(a)]—as will be discussed later, that luminescence becomes more pronounced at low temperature. This luminescence line has rarely been observed in the literature[14,28,37] and as of yet there has been no assignment of its origin.

The origin of the red luminescence line centered at 1.6 eV, as previously mentioned, has been typically associated with H or N impurities.[23,28] Therefore, we paid particular attention to the red luminescence and how it varied depending on the H concentration of our films. However, due to the high intensity and position of the 3.3 eV UV line, the possibility of second order diffraction having an impact on the emission spectra must be considered. To address this, we inserted a 470 nm filter to remove the UV luminescence, which resulted in the removal of the red luminescence from the spectra, shown in Fig. 1(b). Therefore, for the samples analyzed in this paper, the red emission is determined to be that of second order diffraction of the UV and will not be shown in the luminescence spectra in the later figures.

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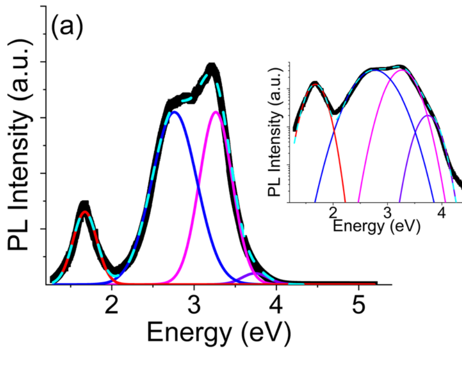

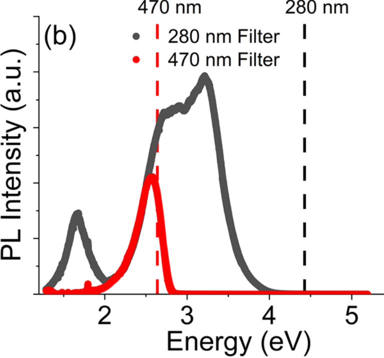

FIG. 1. (a) 290 K PL spectrum of sample C with H concentration ([H] = 1.5 × 10^{17} cm^{-3}). Inset shows the PL spectrum of sample C measured at 290 K in log scale, highlighting the presence of the 3.8 eV peak. (b) 290 K PL spectrum of sample C ([H] = 1.5 × 10^{17} cm^{-3}) with 280 nm filter (black) and 470 nm filter (red).

By analogy to β-Ga_2O_3, UV emission is typically attributed to the recombination of free electrons with STH. One of the reasons for the generation of these STH lies in the composition of the valence band for which the upper state is mainly made up of O 2*p* orbitals, which have characteristics such as small dispersion and large effective masses.[38] The associated holes, with large effective mass, become localized at O sites in the crystal lattice. In β-Ga_2O_3, there are three non-equivalent O sites, two of which have trigonal coordination and one with tetrahedral coordination.[39] According to first principles calculations, the holes tend to localize on the trigonally coordinated sites meaning there are two possible sites for the STHs in β-Ga_2O_3,[39] which is reflected in PL with two bands resolved in the UV region.[22] However, α-Ga_2O_3 has only one type of O site.[39] Therefore, it may be expected that only one luminescence band in the UV region may be attributed to recombination of free electrons and STH, ruling out the assignment of the 3.8 eV line as STH related.

Figure 2(a) shows the PL spectra of all samples measured at 290 K. Apart from the small variation in blue line intensity, all of the 290 K PL spectra were identical. Strong variation across the samples appeared when the temperature was decreased to 9 K, as shown in Fig. 2(b). The PL spectra of sample C with the 480 nm filter and full emission spectrum including red emission is shown in Figs. 2S and 3S, respectively. Figure 2(b) shows a clear enhancement of the 3.8 eV luminescence line with respect to the 290 K measurements. To assess the impact of temperature on the luminescence lines, we looked at the ratio of the integrated intensities of each line measured at 9 and 290 K. We observe a disproportionate enhancement of the integrated intensity of the 3.8 eV luminescence line of samples C and D, which increase by a factor of 18 and 15, respectively, compared to samples A and B where for sample A there is no enhancement of the 3.8 eV luminescence line at 9 K and for B only increases by a factor of 2. From the SIMS measurements shown in Table I, it can be seen that samples C and D have a higher concentration of H and Cl. These impurities are incorporated into the films during the growth process where HCl was used; however, P_0(HCl) is the same for samples B–D. Therefore, the additional HCl should not be the dominant case of the variation in [H] and [Cl]. Rather, we expect $GaCl_x$ and H_2 were the impurity sources because their partial pressures were increased to increase the growth rate. Note that H_2 was produced by the chemical reaction at the Ga container upstream in the reactor (Ga + HCl = GaCl + 1/2H_2). H_2 was also produced by the following reaction GaCl + 2HCl = $GaCl_3$ + H_2. More details can be found in Ref. 36. The variation of the 3.8 eV integrated emission at 9 K with impurity concentration is a strong indicator that this luminescence line is not associated with STH emission, as STH luminescence is assumed to be impurity independent.[22] From theoretical calculations, it is predicted that both H and Cl can act as shallow donors in Ga_2O_3,[31] which would explain the strong correlation of the integrated intensity with temperature.

In order to distinguish between whether H or Cl is responsible, we turn our attention to samples that were grown by plasma enhanced atomic layer deposition (PEALD).[40] The PEALD growth process involves the use of triethlygallium [$Ga(C_2H_5)_3$] as Ga precursor, Ar as

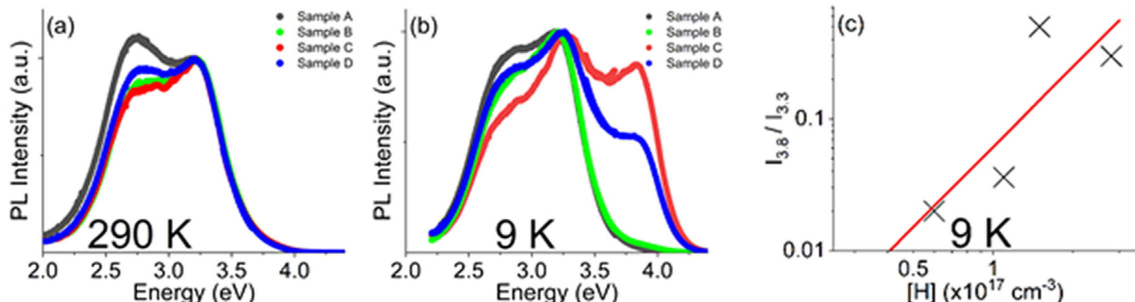

FIG. 2. PL spectra of samples A, B, C, and D measured at (a) 290 K and (b) 9 K. (c) Correlation between the integrated intensity of the 3.8 eV luminescence line and H concentrations of the samples.

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purge gas, and O_2 as plasma source. No Cl is involved in the process, nor in the design of the reactor. The PL spectra of the PEALD samples were measured at 9 K, shown in Fig. 4S in the supplementary material. In this sample, we observe similar emission properties of the 3.8 eV luminescence line in that we observe low, barely distinguishable emission at 290 K and then a strong increase in intensity at 9 K, which leads us to believe the 3.8 eV lines relates to H, and not Cl.

Therefore, we now turn our attention to the role of H in the samples. We observe a strong correlation between the ratio of the integrated intensity at 9 K of the luminescence lines centered at 3.3 and 3.8 eV where the integrated intensity ratio tends to increase with H concentration as shown in Fig. 2(c). We note that the luminescence of sample C is stronger than sample D despite having a lower H concentration. Atomic force microscopy (AFM) and XRD were used to assess whether this variation luminescence could be due to sample quality. AFM data (Fig. 5S) shows that the surface morphology of these two samples are very similar, in terms of topography and roughness. XRD analysis (Fig. 1S) shows that the samples are all phase pure. We note that the main difference between samples C and D is that sample C exhibits a greater tilt (359 arc sec) compared to sample D (103 arc sec). However, these values are still low, and the increased tilt indicates a slightly greater misorientation of the grains, leading to a greater density of grain boundaries and dislocations in sample C, which could have an (still not fully understood) effect on the luminescence. The 3.3 eV emission has already been attributed to STH, which will be invariant of impurities. H incorporates into Ga_2O_3 either on interstitial (H_i) or substitutional (H_O) sites, with both exhibiting low formation energies.[33] Therefore, both are likely to exist as shallow donors in Ga_2O_3. Previous work on muonium, which has similar characteristics to H, suggested H is a shallow donor with a donor depth of $15 < E_d < 30$ meV.[41]

We investigated the temperature dependence of the 3.8 eV line, shown in Fig. 3. We can see that the intensity of the line increases dramatically as the temperature decreases below 100 K, while the 3.3 eV line is comparatively less affected by the temperature. Due to the strong overlap between the lines, it would be inaccurate to attempt to extract an activation energy for this line. However, such a temperature dependence is in line with an origin involving a shallow donor with E_d on the order of 10s meV.

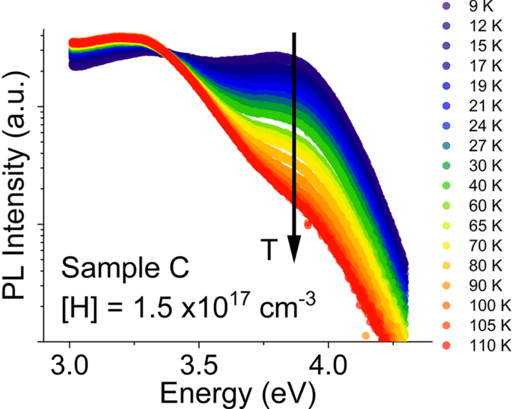

FIG. 3. Temperature-dependent luminescence of sample C measured between 9 and 110 K.

To address the energy emission of 3.8 eV, we require a deep level acceptor to facilitate the recombination from the aforementioned H-related donor. It is well established that it is difficult to identify with absolute certainty the defect involved in the recombination process via PL measurements, even more so in the case where broad, overlapping luminescence lines are involved, such as those shown in Ga_2O_3. However, what we can establish is that there is a strong correlation between the H concentration of the thick films and the integrated intensity of the 3.8 eV luminescence line. It is, therefore, reasonable to suggest that H plays a significant role in the recombination process. As previously mentioned, the interaction of H and V_{Ga} leads to the formation of H-decorated V_{Ga} complexes (V_{Ga}-nH), where n is the number of H atoms involved in the complex defect, Polyakov *et al.* identified a defect energy level positioned 1.3 eV above the valence band maximum.[42] We can tentatively improve on the precision of the number of H atoms involved in the complex vacancy by revisiting the work by Islam *et al.*, which showed that the complex vacancy will be in the acceptor state when 1, 2, or 3 H atoms are bound to the V_{Ga}.[29] To assess the suitability of the V_{Ga}-nH related complex as the acceptor in our DAP recombination model, we use Eq. (1) to calculate the emission energy,

$$h\nu(DAP) = E_g - (E_a + E_d) + \frac{e^2}{4\pi\varepsilon r}, \quad (1)$$

where E_g is the bandgap energy, E_a is the acceptor ionization energy, E_d is the donor ionization energy, the final term on the right of Eq. (1) represents the Coulomb interaction, where e is the charge of an electron, ε is the low frequency dielectric constant, and r is the separation of the donor and acceptor. As a first approximation, the distance r can be given as a function of donor concentration, N_D, given by the following equation:

$$r = \sqrt[3]{\frac{3}{4\pi N_D}}, \quad (2)$$

yielding a donor–acceptor pair separation of 11 nm, assuming the donor concentration is on the order of magnitude of the H concentration, detected by the SIMS measurements, shown in Table I. Using 10 as the relative permittivity of α-Ga_2O_3,[42] $E_d = 15$–30 meV as the shallow donor ionization energy obtained from King *et al.*[41] (in line with our observation of Fig. 3), E_a as 1.3 eV as obtained from Polyakov *et al.*[42] and, finally, $E_g = 5.2$ eV from the transmittance measurements shown in Fig. 6S, we find a DAP emission energy of 3.9 eV that is in excellent agreement with our emission energy obtained experimentally. A schematic of the proposed DAP recombination process is shown in Fig. 4.

The variation of the integrated intensity of the 3.8 eV line with H concentration, along with the identification of the V_{Ga} related complex 1.3 eV above the valence band by Polyakov *et al.*, leads us to believe there is strong evidence of H-decorated V_{Ga} complex that acts as an acceptor in our recombination model.[42] The low formation energy of H related donors, along with the low activation energy strongly favors the incorporation of H as a donor in either H_i, H_O, or V_{Ga}-nH configuration.[29,33,41] However, due to the shallow donor depth, we cannot unequivocally rule out the role of a bound exciton. Further power dependent and time resolved luminescence studies will offer further insight into mechanisms involved in the 3.8 eV emission.

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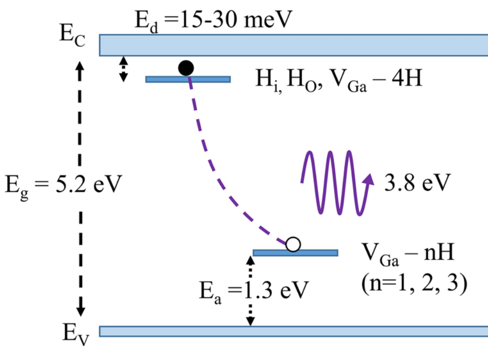

FIG. 4. Model for the 3.8 eV luminescence recombination mechanism. The purple dashed line represents donor–acceptor pair recombination when T < 110 K.

In conclusion, we investigated the optical properties of α-Ga_2O_3 thick films with measurable variations of H and Cl concentrations by means of temperature-dependent PL. The study shows a significant enhancement of UV luminescence band at 3.8 eV at low temperatures, with a strong correlation with the H concentration of the samples. Sample A ([H] $<6 \times 10^{16}$ cm^{-3}) exhibits barely distinguishable luminescence at 3.8 eV even at temperatures as low as 9 K. On the contrary, samples C ([H] = 1.5×10^{17} cm^{-3}) and D ([H] = 2.8×10^{17} cm^{-3}) showed an enhancement in integrated intensity by a factor of 15 and 20, respectively. The strong temperature dependence of the 3.8 eV luminescence line with temperature indicates the role of a shallow donor. Here, we tentatively ascribe the luminescence to DAP recombination where the donor is H related, with possible candidates being H_i, H_O, or V_{Ga}-4H, and the acceptor as V_{Ga}-nH, where n = 1, 2, 3. This study indicates that even small changes in H content of less than 1 order of magnitude can have a significant effect on the UV luminescence properties.

See the supplementary material for a XRD ω-2θ scans, PL spectra with 280 and 470 nm filter, PL spectra of PEALD samples measured at 290 and 9 K, topography maps obtained by AFM, and transmittance measurements obtained using UV-VIS spectroscopy.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

David Robert Lee Nicol: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Yuichi Oshima:** Conceptualization (supporting); Data curation (supporting); Funding acquisition (supporting); Investigation (supporting); Methodology (supporting); Writing – review & editing (equal). **Joe Roberts:** Resources (supporting). **Lewis Penman:** Data curation (supporting); Investigation (supporting). **Douglas Cameron:** Investigation (supporting); Methodology (supporting); Validation (supporting). **Paul Raymond Chalker:** Resources (supporting); Writing – review & editing (supporting). **Robert W. Martin:** Conceptualization (equal); Writing – review & editing (supporting). **F. C.-P. Massabuau:** Conceptualization (supporting); Funding acquisition (lead); Investigation (supporting); Methodology (equal); Supervision (lead); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are openly available in PurePortal at https://doi.org/10.15129/93523e0c-3809-4f8d-ab39-bd029cad054a.

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