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Electronic Supplementary Information

Controlling the interfacial reactions and environment of rare-earth ions in thin oxide films towards wafer-scalable quantum technologies

Authors

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S-1: DLI-CVD Set up [1]

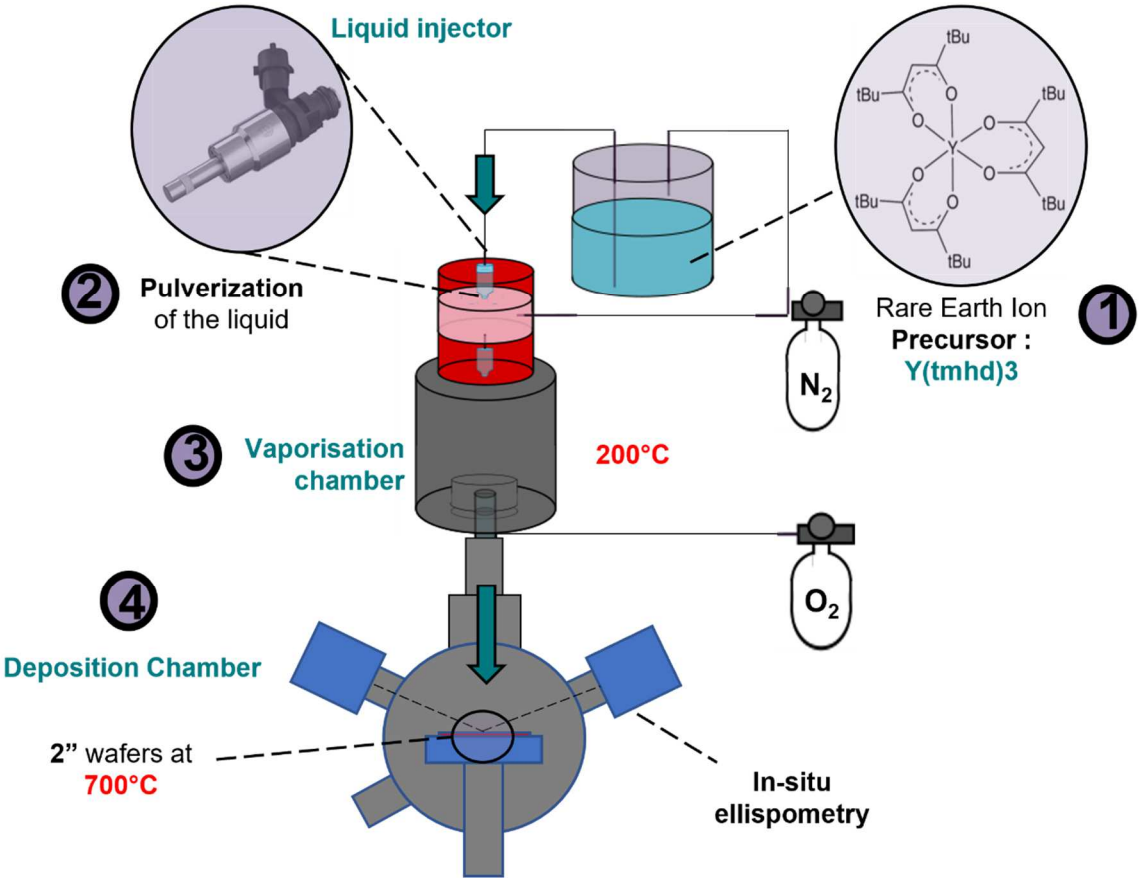


Fig. S1- Direct Liquid Injection Chemical Vapor Deposition set-up.

As described in the article, β-diketonate precursors are used as rare-earth ions source (1). The pulverization of the liquid is done through injectors (2) and the pulsed aerosol is vaporized at 200°C (3). The vapor is carried inside of the reaction chamber towards a 2" Si wafer placed on a sample holder and heated between 600 and 700 °C (4). A control of the temperature is done with a pyrometer calibrated on silicon emissivity (68%). A control of the growth is done by in-situ ellipsometry, which allows to precisely reach the desired thicknesses. To produce the multilayered sample, between each growth layer step, a cleaning step of the chamber under N_2 is realized. Europium contamination in the buffer layers is thus avoided. The gases were pumped with a rotary vane pump allowing the pressure to settle around 10 mbar. Unreacted precursors and chemicals were collected in a nitrogen-cooled trap placed downstream the chamber.

S-2: Interface improvement

We showed on REF [1] that the films deposited on as-received silicon wafers (cleaned with ethanol and acetone in an ultrasonic bath) lead to less textured Y_2O_3 films than the films obtained on silicon samples that underwent the well-established RCA cleaning protocol. Indeed, this step aims at forming a reproducible and good quality chemical oxide on the surface.

For this article we tried to improve further the texture of the film by implementing another step to the chemical cleaning. The deposition on chemically cleaned Si wafer is compared to that obtained on chemically cleaned silicon samples that underwent an additional thermal step in RTA oven. The Si substrate was placed inside an *AS-ONE* Rapid Thermal Annealing (RTA) furnace from *Annealsys* where a 15°C/s ramp is applied followed by a 10 s step at 1100°C under oxygen atmosphere in order to build a 10 nm dense and stable thermal silicon oxide. The samples with two different surface preparations were introduced together in the reaction chamber. Characterization of the film with TEM pictures and XRD are presented below.

a) TEM picture

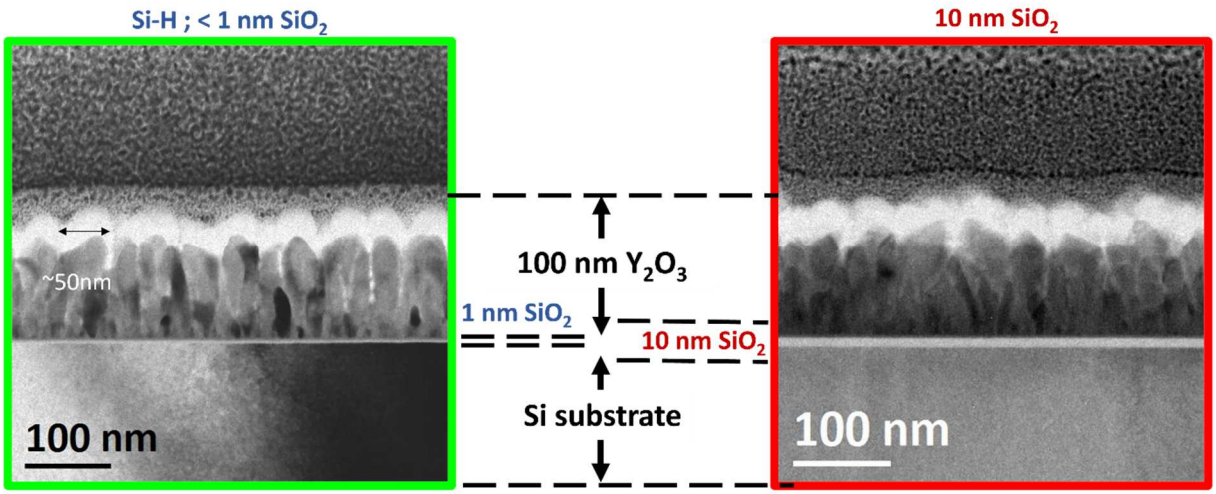


Fig. S2- a) TEM cross-section pictures of film deposited on the two differently treated substrate. In green just the chemical cleaning, in red the chemical cleaning followed by thermal treatment.

The film's thickness was 100 nm. The effect of the surface preparation is noticeable by looking at the interface with the substrate: the chemically cleaned surface has a SiO_2 interface of less than 1 nm whereas the chemically cleaned and thermally annealed surface has 10 nm of SiO_2. Y_2O_3 columns are also visible for the two cases with the same grain sizes on top of the film of about 50 nm. However one can notice that there is less porosity for the film with the thick silicon oxide inter-layer. The thick SiO_2 interface thus seems to improve the film's quality by leading to a less porous film.

b) XRD

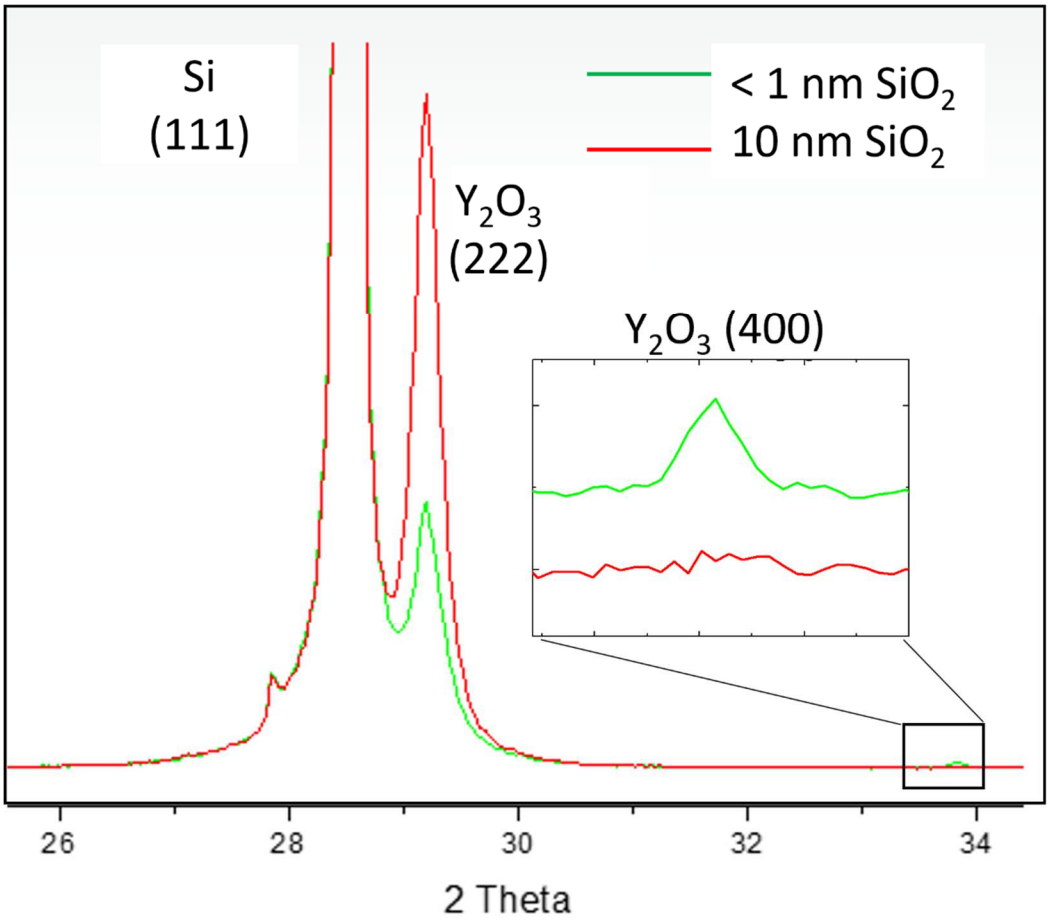


Fig. S2 – b) XRD of film deposited on the two differently treated substrate. In green just the chemical treatment, in red the chemically cleaned followed by thermal treatment.

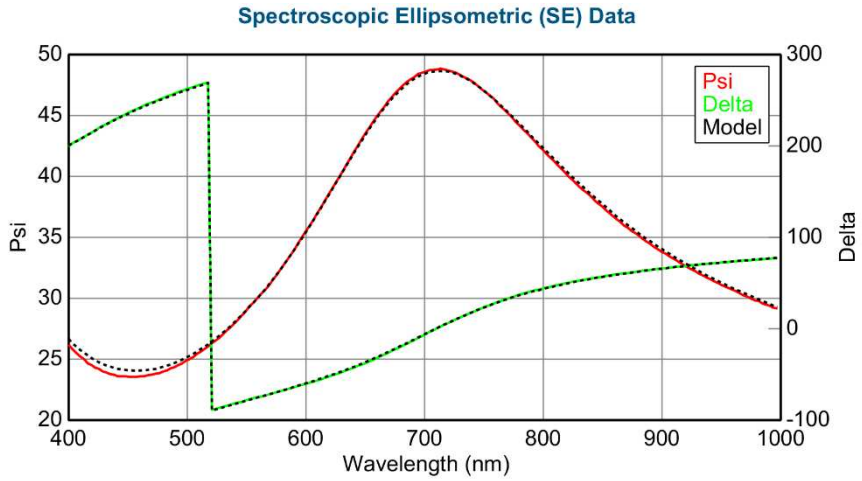
Both surface preparations lead to cubic Y_2O_3 on (111) Si wafer. The intense peak at 28.9° comes from the Si (111) substrate. Both films are textured in this [111] direction as the [222] peak of cubic yttria is the highest one near 29.1°. However, a small signal of the [400] at 33.9° is visible only for the sample with just chemical preparation. The presence of the 10 nm SiO_2 helped to increase the texture of the film [2,3].

S-3: Annealing and Ellipsometry

Ellipsometry is used to determine in and ex situ the thickness and optical properties of the films.

Polarized white light is sent to the sample and after reflection, its phase and amplitude are modified. Delta and Psi parameters are then plotted and, with appropriate fitting models, an estimation of the yttria and interfacial silicon oxide film thicknesses can be evaluated.

First figure S3-a) is the SE of a film after deposition. The model is made of 3 layers: the Si substrate, the SiO_2 inter layer and the Y_2O_3 film. The SiO_2 thickness was measured before deposition and is considered fixed during the deposition process. It was of 12 nm (because of chemical and thermal treatment of the substrate, see S-2). The only fitted parameter is the yttria's thickness. The thickness was fitted using a tabulated model of Y_2O_3 material (Sellmeier).



Yttria thickness (Sellmeier)	SiO_2 thickness (Sellmeier)	Si (substrate)
93.07 nm	11.97 nm	/

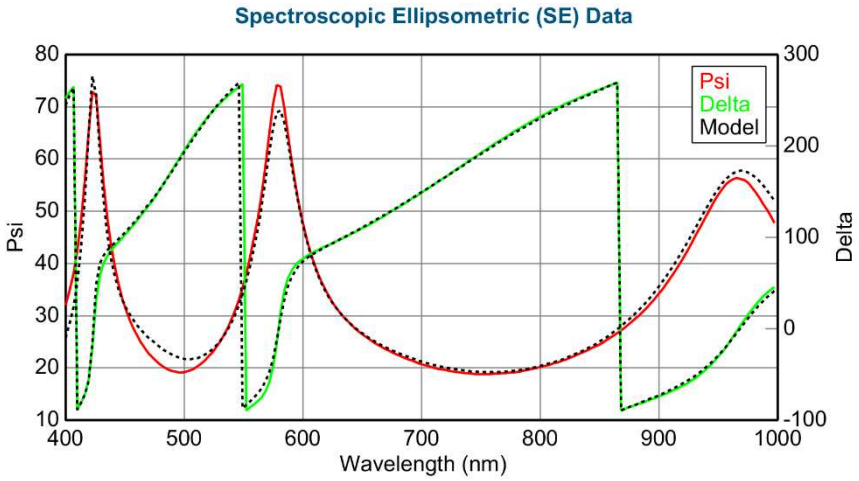
Fig.S3-a) Ellipsometry data. Red and green curve are the experimental ellipsometry parameters Psi and Delta respectively. Dotted black line is a fitted model to the experimental data with fitted parameters mentioned in the table in bold.

A thickness of 93 nm is found for this sample before any annealing.

The sample was then annealed in STA system under air for 2h. As we showed in TOF-SIMS (Fig 2 in the article), diffusion of Y, Si and O is expected after annealing. The previous 3 layers model does not apply in this case. The model used for fitting the data here is made of two layers: the Si substrate and a mathematical model for the intermixing layer. The model used to fit the measured Ψ and Δ data is a Cauchy model, where the refractive index of the thin layer is described by a mathematical equation as:

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

In addition, some roughness was added to the model. The ellipsometry data are presented below with the list of the fitted parameters.



Roughness (nm)	Intermixing	layer	(Cauchy	model)	Si (substrate)
	A	B	C	Thickness	
21 nm	**1.798**	**-0.01455**	**0.003**	**471 nm**	/

Fig. S3-b) Ellipsometry data after 1200°C annealing in STA. A strong change of the spectrum is observed with the apparition of new oscillations for delta and psi. Dotted black line is a fitted model to the experimental data with fitted parameter mentioned in the table in bold.

New oscillations (interference fringes) appear on both spectra which is attributed to a thickening of the film. A strong thickening of the layer is observed [4] with at the end a 471 nm of intermixing layer. This is in good agreement with TOF SIMS results shown in the article where a total etching of 500 nm was necessary to reach the substrate SE is here used as a relevant daily and easier indicator of thickening of our films after annealing treatment compared to a TOF-SIMS platform (UHV etc…).

S-4: Post-annealing of the film, complementary data

a) SOA 1300°C on ABC sample

In the article we showed that for the simple active layer A, new phases appeared at 1100°C. Using the a buffer layer with the ABC sample, the apparition of new phases were observed for annealing at 1200°C.

Here we plotted the map of ABC sample (buffer + cap) under STA annealing at 1300°C in air for 2 hours.

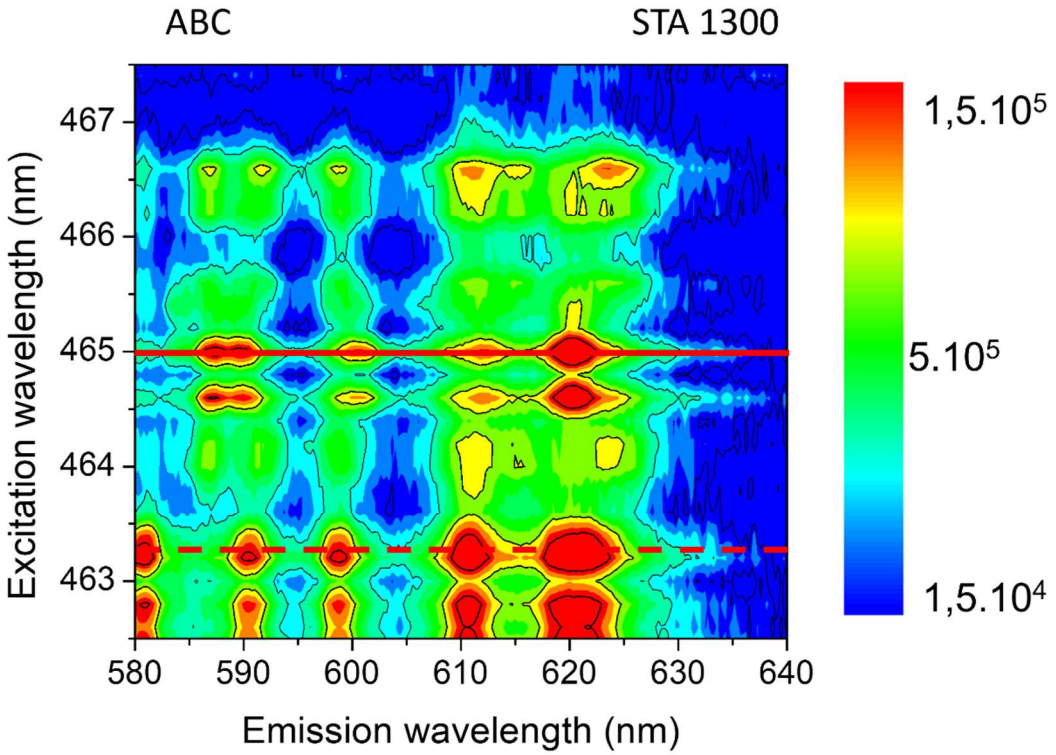


Fig. S4- a) 2D-PLE map recorded around the excitation wavelength of $^7F_0$-$^5D_2$ Eu transition for the ABC sample annealed in STA at 1300 °C. The full and dotted lines correspond to the 465 nm and 463.4 nm excitations respectively which spectra are presented in the article Fig. 3-d.

The maximum signal here is ten time smaller than that of the other annealed samples. There is therefore a strong loss of fluorescence because of this strong annealing. The formation of new phases at 1300°C leads to new environment [5,6], defects for europium ions that are reducing its fluorescence.

There is a strong change of the map's shape with the apparition of broad peaks both in emission and excitation. At this temperature, the yttria film is no more cubic but a mix of other silicate phases.

b) Annealing with RTA

Another annealing system was used in this study which results are partially presented in the paper. Rapid Thermal Annealing of the sample was done using very fast ramps of heating and cooling (15 °C / s) and short time of annealing (10 s). PL results of RTA at different temperatures are presented for the simple active layer A in Fig 4-b)i. and for the buffered film ABC in Fig 4-b)ii.

i. Single layer A under RTA

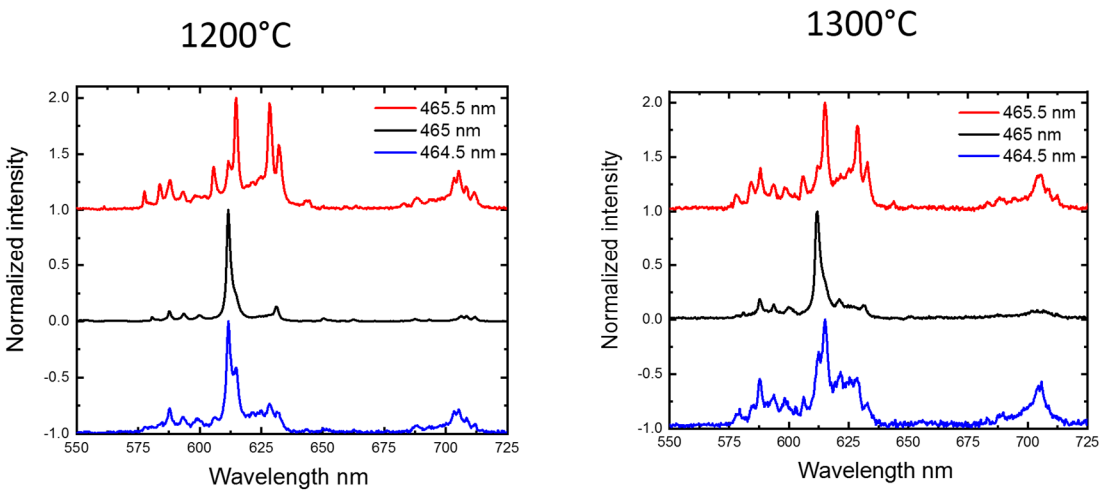


Fig. 4-b-i) Photoluminescence spectra of the single active layer A annealed at 1200°C and 1300°C in RTA. Emission spectra are recorded around the resonant excitation wavelength of the $^{7}F_{0}$-$^{5}D_{2}$ Eu transition at 3 wavelengths 465.5 nm, 465 nm and 464.5 nm.

When the sample is annealed at 1200°C typical europium emission spectrum is observed when exciting with 465 nm wavelength. However, a change of the spectra is already observed when exciting at another wavelength like 464.5 nm. Contrary to STA, no changes of the spectra were observed for a 1100°C annealing. This is a 100°C improvement before a deformation of the spectra. The annealing is done in a very short time and thus reduces the species' diffusion. Therefore, higher temperature of annealing could be reached without a to strong change of the spectra. 1300°C still remains our upper limit for annealing whatever the system as the spectra are modified, even with the RTA.

ii. Multi-layer ABC under RTA

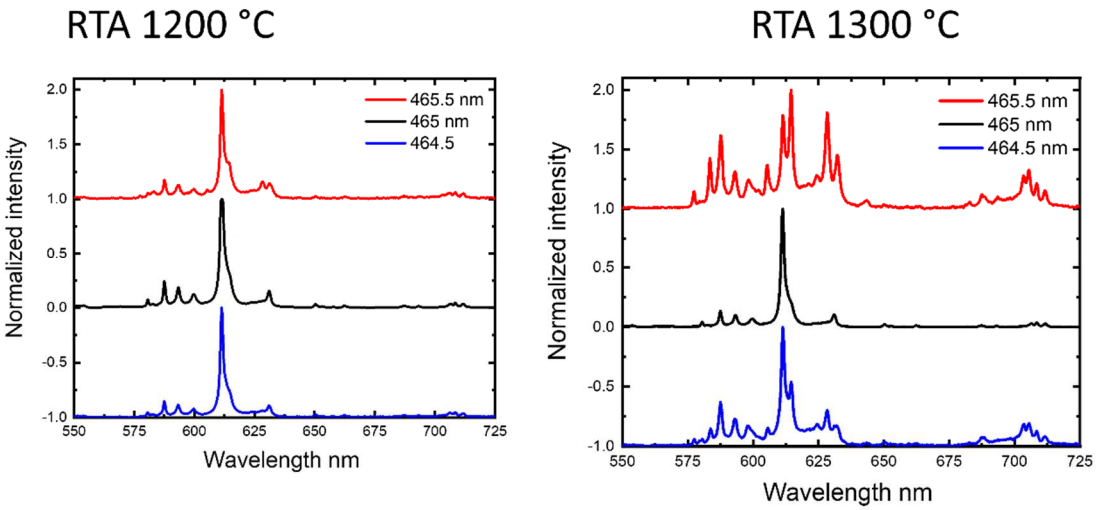


Fig.4-b-ii) Photoluminescence of the multi-layered sample ABC annealed at 1200°C and 1300°C in RTA. Emission spectra are recorded around the resonant excitation wavelength of the $^{7}F_{0}$-$^{5}D_{2}$ Eu transition at 3 wavelengths 465.5 nm, 465 nm and 464.5 nm.

The effect of multilayering is clearly visible here. Even at 1200°C no clear change of the spectra shape is seen even using different excitation wavelength. The buffer layers efficiently protect the active layer containing the emitting ions at 1200°C when the RTA is used. However annealing at 1300°C shows a strong change of the spectrum shape when exciting at for example 465.5 nm. Whatever the annealing system, 1300°C still is our upper limit before the formation of parasitic phases [7].

S-5: Hole burning experiment on different samples and annealing conditions

The hole burning contrast have been determined by the following formula:

$$\frac{\int Ifluo\ without\ burn\ pulse - \int Ifluo\ with\ burn\ pulse}{\int Ifluo\ without\ burn\ pulse} \times 100$$

Where $Ifluo$ is the Eu ions red fluorescence intensity ($^5D_0$ – $^7F_2$ transition) recorded with the probe pulse in the absence or presence of a burning pulse (see article Fig.7-a). This value gives an inset of the burning efficiency of all the Eu ions excited at a specific frequency inside the inhomogeneous linewidth Γ_{inh}.

Spectral hole width and burning contrast of all three samples A, ABC and D described in the article and annealed under different conditions (STA, RTA, atmosphere, duration) are presented below in Table S-5.

Sample	**Post-annealing**			**Burning contrast of the spectral hole (%)**	**Spectral hole width at 3 K (MHz)**
	Temperature (°C)	**Duration (min)**	**Atmosphere**		
A	X	X	X	X	**No SHB**
TAC	X	X	X	49	**23**
TAC	STA 1100	120	Air	66	**18**
TAC	STA 1200	120	Air	57	**17**
TAC	STA 1200	720	Air	X	**No SHB**
TAC	RTA 1200	5	O_2	42	**20**
TAC	RTA 1300	5	O_2	10	**35**
TAC	STA 1200 + RTA 1200	120 + 5	Air + O_2	55	**20**
TAC	STA 1200 + RTA 1300	120 + 5	Air + O_2	38	**23**
TAC	RTA 1300 + STA 1200	5 + 120	O_2 + Air	X	**No SHB**
E	STA 1100	120	Air	52	**15**
E	STA 1100	120	Argon	21	**25**
E	STA 1100 + STA 600	120 + 120	Argon + O_2	56	**10**

Table S-5: Γ_{hole} and hole burning contrast for different samples and post-annealing conditions. Double step post annealing were sometimes applied, the first value being related to the first post-treatment. Blue lines are samples and values presented in the article Figure 7 and the orange line in Figure 8. Single active layer is labeled A, thin multilayer is ABC and thick multilayer is D.

As presented in Fig.7-a in the article, without a buffer layer no spectral hole is observed. With the presence of 80 nm buffer layer, a 23 MHz hole with 49 % contrast is measured. Using STA post annealing, Γ_{hole} is narrowed by 20% to reach 17 MHz and the contrast is also improved. However, when annealing during a longer time (6 hours), no holes were detected confirming the strong Si^{4+} diffusion induce disorder. As diffusion is ruled by the annealing temperature and its duration, the longer the sample is annealed, the more Si^{4+} are in the active layer. Despite the strong broadening in inhomogeneous linewidth, RTA post-treatment (orange rectangle in Fig.6-b) allow the burning of spectral holes but with a smaller contrast than with STA. At 1300 °C, RTA annealing shows the smallest contrast which is in good agreement with the formation of new phases at this temperature. Two steps annealing using both rapid and slow system were also investigated on ABC sample without improvements and even sometimes without burning spectral holes. Different annealing conditions were tried on the thick sample D (under air, under argon), which best result was obtained for the double step STA annealing first under argon at 1100 °C then under O_2 at 600 °C.

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