# Ag+↔Na+ ion exchanged silicate glasses for solar cells covering: down–shifting properties.

E. Cattaruzza[a,*], V.M. Caselli[a], M. Mardegan[a], F. Gonella[a], G. Bottaro[b], A. Quaranta[c], G. Valotto[d], F. Enrichi[e]

[a] Nanobiomaterials and Nanosciences Center, Molecular Sciences and Nanosystems Department, Università Ca' Foscari Venezia, via Torino 155/b, 30172 Venezia–Mestre (Italy)

[b] Institute for Energetics and Interphases, National Research Council (IENI–CNR) c/o Dept. of Chemical Sciences, Padova University, via F. Marzolo 1, 35131 Padova (Italy)

[c] Department of Industrial Engineering, University of Trento, via Mesiano 77, 38123 Trento (Italy)

[d] Environmental Science Informatics and Statistics Department, Università Ca' Foscari Venezia, Dorsoduro 2137, 30123 Venezia (Italy)

[e] Veneto Nanotech, Via Delle Industrie 5, Marghera, Venice 30175 (Italy)

* Corresponding author. Tel.: +39 041 2346716. E–mail address: cattaruz@unive.it (E. Cattaruzza).

## Abstract

The suitability of the Ag+↔Na+ ion exchange process was tested for the production of luminescent cover glasses with down–shifting properties suitable for solar cells. The photoluminescence properties were investigated as a function of the preparation parameters (i.e., Ag salt bath concentration, post–synthesis annealing temperature and duration). The performance of the samples was tested by measuring the output power of a Si solar cell covered with the treated glass slides and exposed to a solar simulator radiation; the photoluminescence quantum yield of the best performing samples was also estimated.

## 1. Introduction

In the research field aimed at improving the physical efficiency of the photovoltaic cells, one of the most promising actions is the study of the synthesis of materials able to modify the solar spectrum in an effective way for the radiation–current pulse conversion. Actually, about the 8% of the total power coming from the Sun onto the Earth surface lies in the near–ultraviolet range (E ≥ 3.0 eV, or λ ≤ 400 nm) [1], a region for which both the wafer–and the thin film–based devices exhibit a limited energy conversion efficiency [2]. In general, modification of the sunlight radiation by luminescence down–shifting, up–conversion, down–conversion and/or their combination play a crucial role in overcoming the problems related to the conventional Si–based modules technologies. Down–shifting materials, absorbing high–energy photons and converting them in low–energy ones, can be obtained by doping the cover glass of the solar cells with suitable luminescent elements. Recently, the possibility to use the ion exchange process for this purpose was successfully explored: samples doped with Cu+ ions exhibited an encouraging down–shifting behaviour, demonstrating to be suitable for improving the efficiency of a GaAs solar cell [3]. However, the doping of the same silicate glass with Ag+ did not give comparably

interesting results [3], in spite of the evident down–shifting potential. As a matter of fact, silver–doped silicate glasses exhibit broad luminescence bands around 350 nm, due to isolated emitting $Ag^+$ ions, and around 430–450 nm, ascribed to $Ag^+$–$Ag^+$ pairs, whose intensity increases with the post–synthesis annealing temperature [4, 5 and refs. therein]. Moreover, a broad band peaked around 600 nm appears after post–exchange thermal treatments, due to the formation of $(Ag_3)^{2+}$ trimers or similar very small multimers [4, 5 and refs. therein]. Indeed, all these bands are excited by radiation in the UV and near–UV regions. The main reason for the unsatisfactory performances of the Ag–doped cover glass is that in the as–exchanged samples the surface reflectance counterbalances the luminescence yield, lowering the final cell output power. Samples subjected to thermal treatments after ion exchange gave poor results as well [3], even if they were characterized by broad luminescence bands in the visible range. In this work, a systematic experimental study of both photoluminescence and absorption properties is presented for silicate glasses doped with silver by the ion exchange process, by varying the preparation parameters such as salt bath concentration, post–treatment annealing temperature and duration. The glass optical response, in terms of both luminescence and absorption properties, can be controlled by a proper definition of the thermal treatment protocol after the doping, aimed at increasing the formation of silver dimers, trimers and very small clusters, and preventing high concentrations of silver nanoaggregates, detrimental to the glass transparency due to their surface plasmon resonance (SPR) absorption band centred around 400 nm. Simo *et al.* recently showed [6] that for a silicate glass doped with silver by ion exchange, a post–treatment annealing threshold temperature $T_{th}$ actually exists: for annealing at $T<T_{th}$, only molecular clusters and small charged aggregates (diameter <1 nm) are formed, most likely silver dimers. On the other hand, for annealing at $T>T_{th}$, these aggregates grow to nanoparticles (diameter >1 nm), with number and size depending on the annealing duration and on the number of atoms acting as reducing agent. For the soda–lime silicate glasses used by Simo *et al.*, the determined threshold temperature for annealing in air was $T_{th}=410°C$. Therefore, the determination of the threshold temperature for our Ag–doped glasses appears to be the way to maximize their down–shifting properties, by a suitable treatment after the ion exchange.

## 2. Experimental

Ion exchange was performed on 1 mm thick slides of "tin–free" soda–lime silicate glass, with atomic % composition: 59.6 O, 23.9 Si, 10.1 Na, 2.6 Mg, 2.4 Ca, 0.7 Al, 0.5 K, 0.2 S, plus Ti and other elements in traces. The choice of a glass not produced by the usual floating process prevents the problems related to the presence of tin on one side of the glass, which may act as a reducing agent, thus favouring the silver precipitation [3]. Glass slides were prepared by a four–step cleaning process in ultrasonic baths (deionized $H_2O$; trichloroethylene; acetone; isopropyl alcohol). Silver ions were introduced in the glass by immersion of the slides in a molten salt bath of $AgNO_3/NaNO_3$, with two different molar ratios of silver nitrate (1 % and 0.1 %) In the following, we will refer to these two doped glasses as 1 % and 0.1% samples, respectively, whereas in the discussion we will focus on the glass exhibiting the best features, namely, the 1%. The ion exchange was performed in air at 320°C, for 60 min., giving a silver atomic concentration at the glass surface of about 6 % and 1.5 % for the 1% and 0.1% glasses, respectively, as determined by Rutherford backscattering spectrometry [7]. The estimated thickness of the silver–containing layer was about 15 μm. Annealings in air were realized after the silver doping at three temperatures (380, 410, and 440°C) and for three duration times (1, 4, and 16 h). UV–VIS optical absorption (OA) spectra were recorded with an Agilent 8453 spectrophotometer in the

280–650 nm region. Photoluminescence (PL) and excitation (PLE) spectra were collected with a Fluorolog–3 (Horiba–Jobin Yvon) modular system equipped with a 450W Xe lamp coupled to a double monochromator for the excitation wavelength selection ($\lambda_{exc-1}$=260 nm, $\lambda_{exc-2}$=350 nm). Absolute photoluminescence quantum yields (PLQY) were calculated from corrected emission spectra data, obtained from an apparatus consisting of a Spectralon® coated integrating sphere accessory (4", F–3018, Horiba Jobin Yvon), fitted in the fluorimeter sample chamber. We used $\lambda_{exc-2}$=350 nm as the exciting source, measuring the emission yield in the 380–750 nm wavelength range. Three independent measurements were carried out on each examined sample to estimate the PLQY reproducibility and uncertainty. The final relative uncertainty of the PLQY data is estimated to be around 10–20 %, a value typical of measurements procedures that are extremely sensitive to intrinsic systematic errors.

The solar simulator system used for measuring the power delivered by a Si solar cell covered with the samples was made of a DC power supply, a halogen dichroic reflector lamp DECOSTAR 51 ECO SST 14W 12V 36 GU5.3 (Osram) as light source without UV filter, a solar panel, and a digital multimeter (Tektronix Keithley 2410). The DC supply was directly linked to the lamp and a multimeter was connected to the cell. The light source was hold on the top of an iron structure, and the cell was placed under the light source at 14 cm of distance. The solar cell used in this apparatus is a $2\times1$ cm$^2$ Si–based commercial device. The cover sample was put without matching fluids on the Si cell and the power–against–voltage P–V curve was obtained by simultaneously measuring the flowing current I and the cell voltage V (P=V×I). A specific data acquisition procedure was adopted to minimize fluctuations: for each sample, the curve was measured several times by removing and putting again the glass slide on the cell. This procedure was repeated several times during the different measurement runs, to take also into account the fluctuation of the light source. The final estimated uncertainty was found to be lower than 0.5 % of the measured power values.


## 2. Results and discussion

### 2.1. Optical absorption (OA)

Due to the low amount of silver, the absorption spectra (not reported) of all the annealed samples prepared with the 0.1 % molar concentration of silver nitrate are equal to the spectrum of untreated glass, within the experimental uncertainties. On the contrary, the samples prepared with the Ag–richer salt bath exhibits an absorption evolution as a function of the annealing parameters. Therefore, in the following discussions we will focus on the 1 % glass. As expected, the changes are more relevant for annealing at higher temperatures and longer times. In Fig. 1, the modifications induced by the annealing in 1 % glass OA spectrum are shown for the samples annealed at 440°C: the spectra exhibit an absorption band around 350 nm, due to the presence of a high number of sub–nanometric (neutral and/or charged) silver aggregates [6, 8], whose formation is favoured by the relatively high annealing temperature. The spectra for the samples annealed at 380 and 410°C (not reported) are characterized by a lower optical absorption, with a broad shoulder at about 360 nm, as expected from the results reported by Simo *et al*. [6]. In the perspective of using these glasses as cover for PV cells, a good transparency is mandatory, so the question of finding the optimal compromise between the absorption and the prescribed functional properties remains open. The presented results however show that the absorption features of the considered glasses may be controlled also by properly tuning the heat-treatment procedures.

## 2.2. Photoluminescence emission and excitation (PL and PLE)

The luminescence shown by exciting at $\lambda_{exc-1}$=260 nm the 1% samples (Fig. 2) is the typical observed in Ag–doped silicate glasses (see for instance [3]), characterized by a large band centred at about 430 nm, related to the presence of $Ag^+$–$Ag^+$ pairs. It is interesting to note that in these glasses the band around 350 nm of isolated emitting silver ions is not present, unlike the spectra for samples exchanged at 0.1 % (not reported). In fact, in 1 % samples the high concentration of silver lowers the probability to find a detectable amount of isolated emitting ions after the annealing. Moreover, by annealing at increasing temperatures and times, also the band related to silver multimers and centred at about 600 nm becomes relevant, since the temperature and the duration of the annealing favour the aggregation of silver. In particular, the sample with the highest integrated emission intensity is the 410°C–16 h.

From the point of view of using these glasses as PV cover, more interesting is the PL behaviour at $\lambda_{exc-2}$=350 nm, i.e., a near–UV radiation which can actually strike a PV panel on the Earth surface [1]. In Fig. 3, the PL curves for all the 1 % samples are characterized by a single wide band around 550–600 nm, due to silver multimers. At a fixed temperature, the intensity of this band increases with the annealing time, reaching its maximum value for the 410°C–16 h sample; however, also the 440°C–4 h and the 410°C–4 h samples exhibit high intensities. The (not reported) PL spectra of the 0.1 % samples, recorded at $\lambda_{exc-2}$=350 nm, exhibit a wide band centred between 550 and 600 nm, too, with intensity–dependence similar to the 1 % samples; in addition, the band around 430 nm remains visible, though with very low intensity. This is related to the lower Ag concentration for these samples, allowing the presence of a detectable fraction of silver dimers with respect to the other silver aggregates.

The PLE spectra for the 1 % samples are reported in Fig. 4, where the excitation curves are recorded by fixing the emission wavelength at 630 nm, i.e., near the maxima of the PL curves shown in Fig. 3. As can be observed, the excitation bands are in the near–UV region, namely, within the 300–400 nm range, thus proving that these glasses can act as down–shifters in the visible range.

## 2.3. P–against–V cell test

Fig. 5 shows the Si cell output power around its maximum region, plotted as a function of the voltage, using the undoped glass and the 10 samples of the 1 % glass (the as–exchanged and the nine annealed ones). The same test with the 0.1 % glass (not reported) did not indicate detectable differences among samples, being all the recorded P–V curves equal to that of the pure glass. In Fig. 5, the curve obtained by the pure glass shows that none of the Ag–doped glasses is so far suitable for increasing the cell yield if compared to the undoped glass. However, an interesting trend is outlined, addressing the way to improve the glass performance by more suitable post–synthesis treatments. In fact, the P–V curves show that two samples have a lower yield than the as–exchanged one: the 440°C–4 h and the 440°C–16 h samples. This "bad" behaviour is related to the remarkable loss of transparency due to the formation of sub–nanometric silver aggregates. As far as the other samples are concerned, all those annealed for different times at 380°C exhibit a very similar behaviour. The annealing temperature is probably too low to increase significantly the formation of silver dimers and trimers, and the consequent PL emission useful to the down–shifting. In the frame of the Simo *et al.* model, we may assume that the threshold

temperature $T_{th}$ is close to 410°C also for our Ag-doped soda–lime silicate glass. So, annealing below this temperature prevents the formation of large absorbing clusters, detrimental for the cell yield, giving rise to a very large fraction of silver dimers (and/or trimers and/or few–atoms aggregates) for longer treatment times.

In order to estimate the right value of the $T_{th}$ for our 1 % glass, we studied the integrated PL intensity as a function of the T and t values. In particular, we evaluated the 400-700 nm integrated PL intensity I (detected for $\lambda_{exc-2}$=350 nm) of the nine annealed samples, then fitting the calculated I(t,T) data by using different smoothing functions, so obtaining 3D surface plots through the software Statistica 8.0 [9]. In Fig. 6, the 2D projection of a 3D surface plot is reported, obtained by using the bi-cubic spline smoothing procedure. For further details, see for instance [10,11]. It is evident that the most promising annealing conditions to maximize the 350 nm PL emission should be a temperature T in the 405–420°C range, for a duration time in the range from 9 to 12 hours. Similar fits made with other smoothing procedures based on different polynomial regression algorithms (such as the distance-weighted least square and the negative exponentially-weighted fittings) gave comparable results. Although the experimental points are limited in number and not homogeneously distributed in the (t,T) plane, the obtained estimations are in agreement with the reported experimental findings. Starting from these results, the work in progress is a more refined experimental investigation in the best identified (t,T) region.

*2.4. Photoluminescence quantum yield (PLQY)*

Table 1 shows the PLQY values measured at $\lambda_{exc-2}$=350 nm (emission range 380–750 nm) for the most interesting 1 % samples. The PLQY value of the as–exchanged sample is 2 %. The thermal treatments increase the PLQY as a consequence of the formation of Ag luminescent aggregates. In particular, samples annealed at 410°C exhibit a relevant increase of the PLQY. It is worth noting that also for short times (1 h), annealing at 440°C gives a good PLQY value; in this case, a short thermal treatment at high temperature induces the formation of luminescent Ag aggregates without significant formation of larger metal clusters. As far as the annealing at 380°C is concerned, the representative sample 380°C–4 h is characterized by an interesting PLQY value: at this temperature the formation of large silver aggregates is prevented, thus favouring the formation of silver luminescent centres. Few data are found in the literature regarding the absolute fluorescence quantum yield of Ag–doped glasses. Among them, Kuznetsov *et al*. [12] measured a PLQY of 20 % at $\lambda_{exc}$=366 nm, and even higher at lower excitation wavelengths. However, the same authors measured values as low as 2 % at $\lambda_{exc}$=340 nm [13]. As explained before, the results strongly depend on the aggregation states of silver, thus very different values can be obtained depending on the synthesis parameters, and this give promising perspectives for a preparation protocol able to indicate a suitable synthesis recipe.

**3. Conclusions**

With the aim at improving the yield of a photovoltaic panel by a suitable tuning of the cover glass properties, we investigated the possibility to exploit the luminescence features of Ag–doped silicate glasses as a way to convert the higher–energy portion of the visible light spectrum into lower energy photons, more easily processed by the conventional solar cells. We tested the $Ag^+\leftrightarrow Na^+$ ion exchange process for the production of luminescent cover glasses having suitable down–shifting properties. An efficient wavelength down–

shifting is favoured by the presence inside the glass of very small Ag aggregates such as dimers, trimers and very small multimers; on the contrary, it is prevented by the formation of larger silver aggregates. In order to tune the formation of the desired aggregates, thermal treatments were needed after the ion exchange. Some preliminary studies were therefore performed on our Ag–doped soda–lime glasses by determining the photoluminescence properties exhibited after thermal treatments in air at different temperature and duration values. The samples were also tested as cover of a Si cell in a solar simulator. Though the examined Ag–doped glasses did not exhibit a significant increase of the total external quantum efficiency of the cell, some suggestions for the improving of the glass properties were obtained by the analysis of the photoluminescence quantum yield. Owing to these results, we determined the possible range for the optimal post–synthesis annealing (405–420°C for the temperature, 9–12 hours for the time) that should allow the production of best–performing Ag–doped samples.

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Figure captions.


Fig. 1.
Optical absorption spectra of 1 % Ag–doped samples annealed for different times at T= 440°C.

Fig. 2.
PL spectra of 1% Ag–doped samples recorded with $\lambda_{exc}$=260 nm. The strong peak centred at $\lambda$=2$\lambda_{exc-1}$ is an instrumental artefact. The annealing parameters are indicated in the labels.

Fig. 3.
PL spectra of 1% Ag–doped samples recorded with $\lambda_{exc}$=350 nm. The annealing parameters are indicated in the labels.

Fig. 4.
PLE spectra of 1% Ag–doped samples. The monitored wavelength is $\lambda$=630 nm. The annealing parameters are indicated in the labels.

Fig. 5.
Zoom on the maximum Si cell output power region of the power–voltage curve. The samples used as cell cover glass are reported.

Fig. 6.
2D projection of a 3D smoothing spline fit of I(t,T) data. I represents the 400-700 nm integrated PL intensitity ($\lambda_{exc}$=350 nm) of the 1% glass after annealing; the white dots indicate the positions in the (t,T) plane of the nine annealed samples.
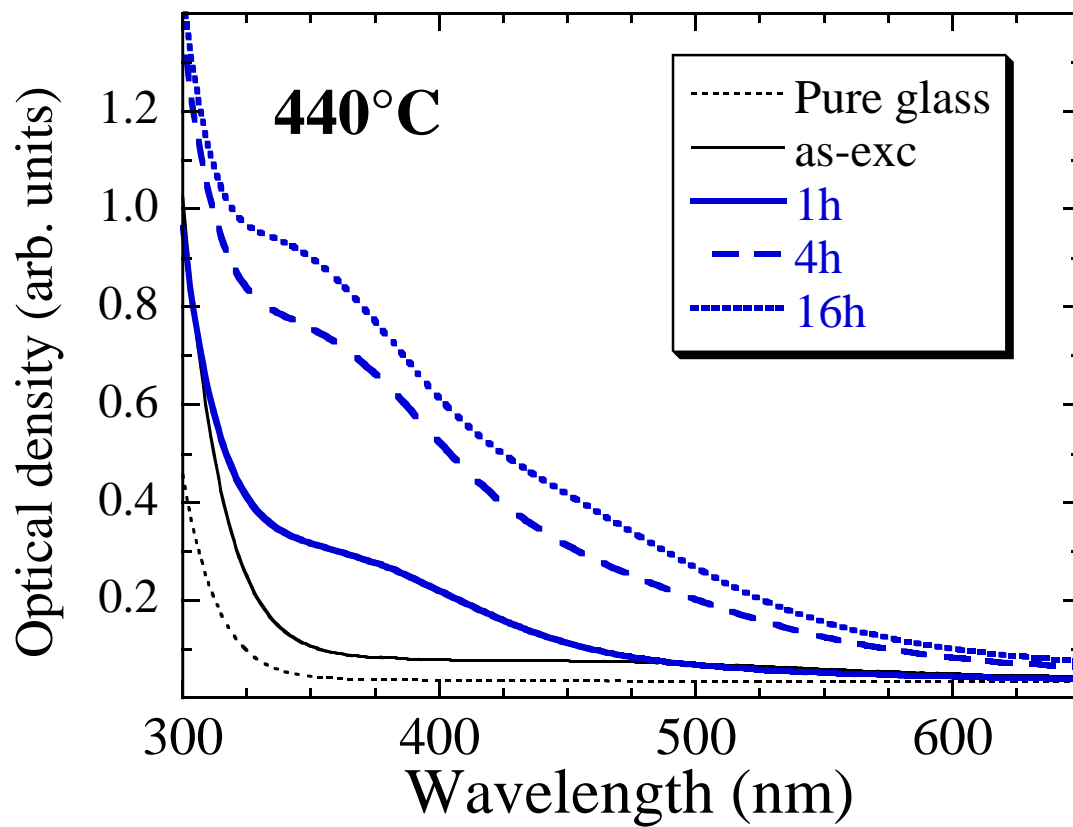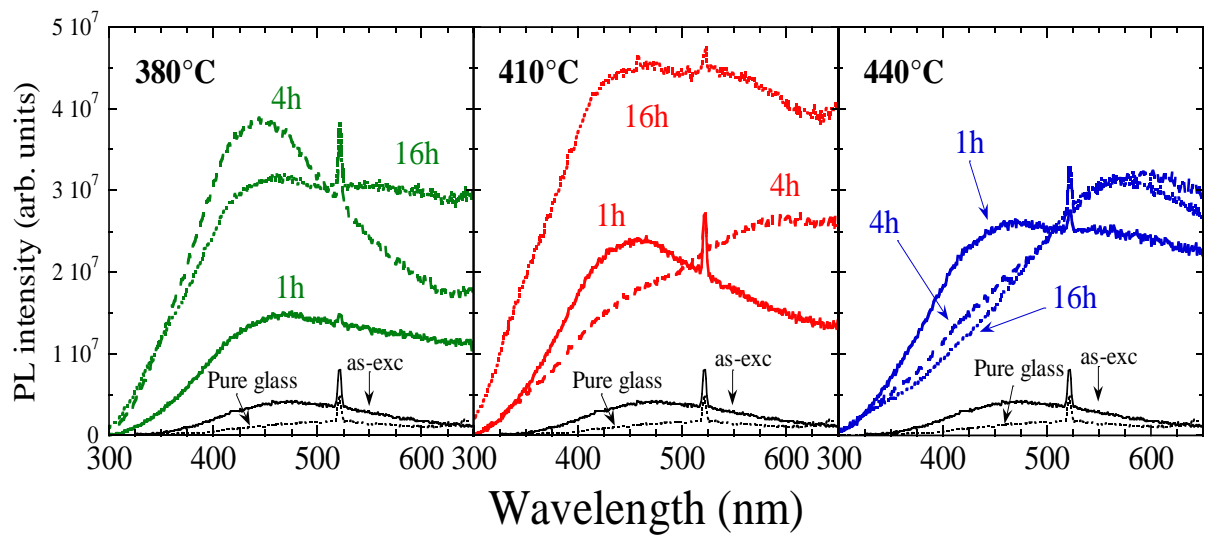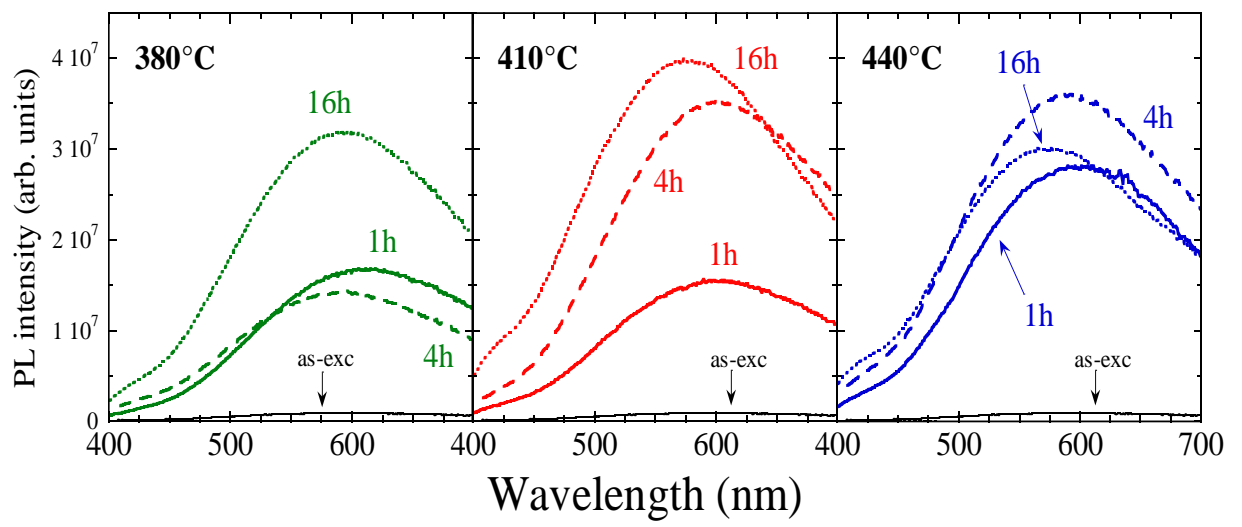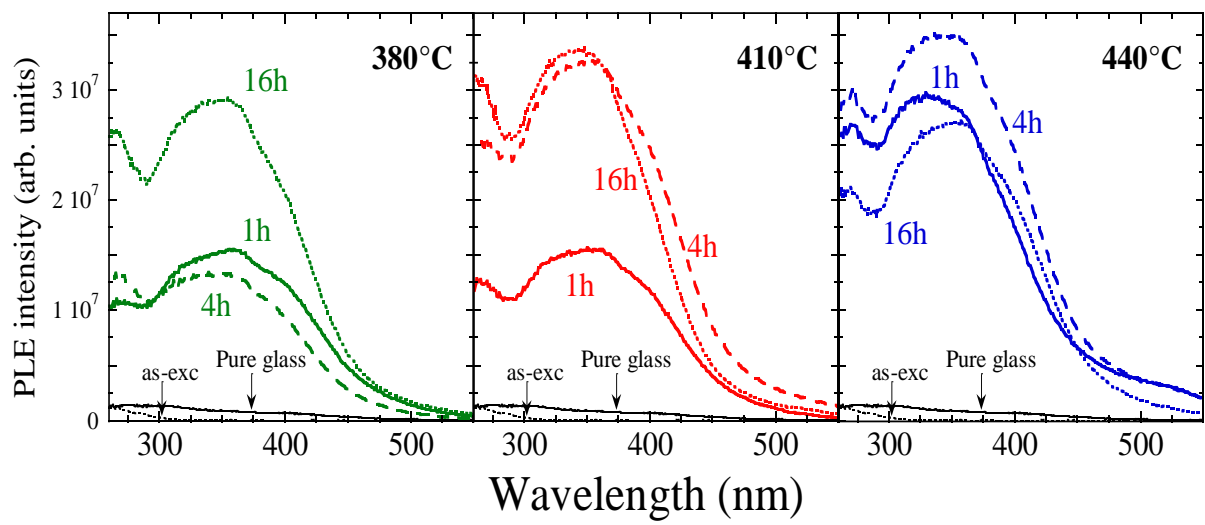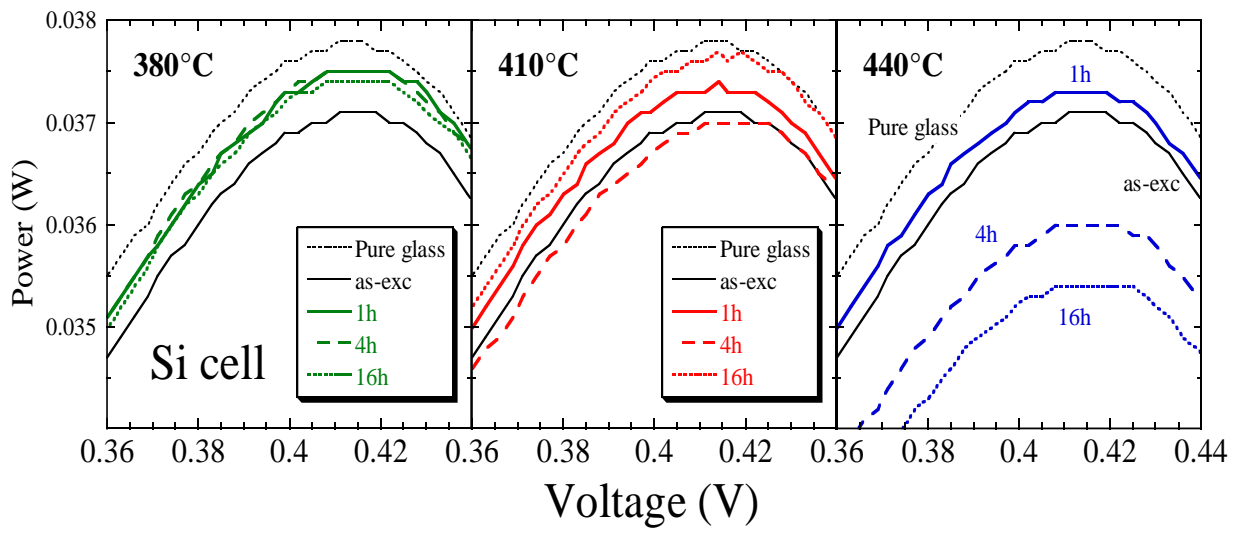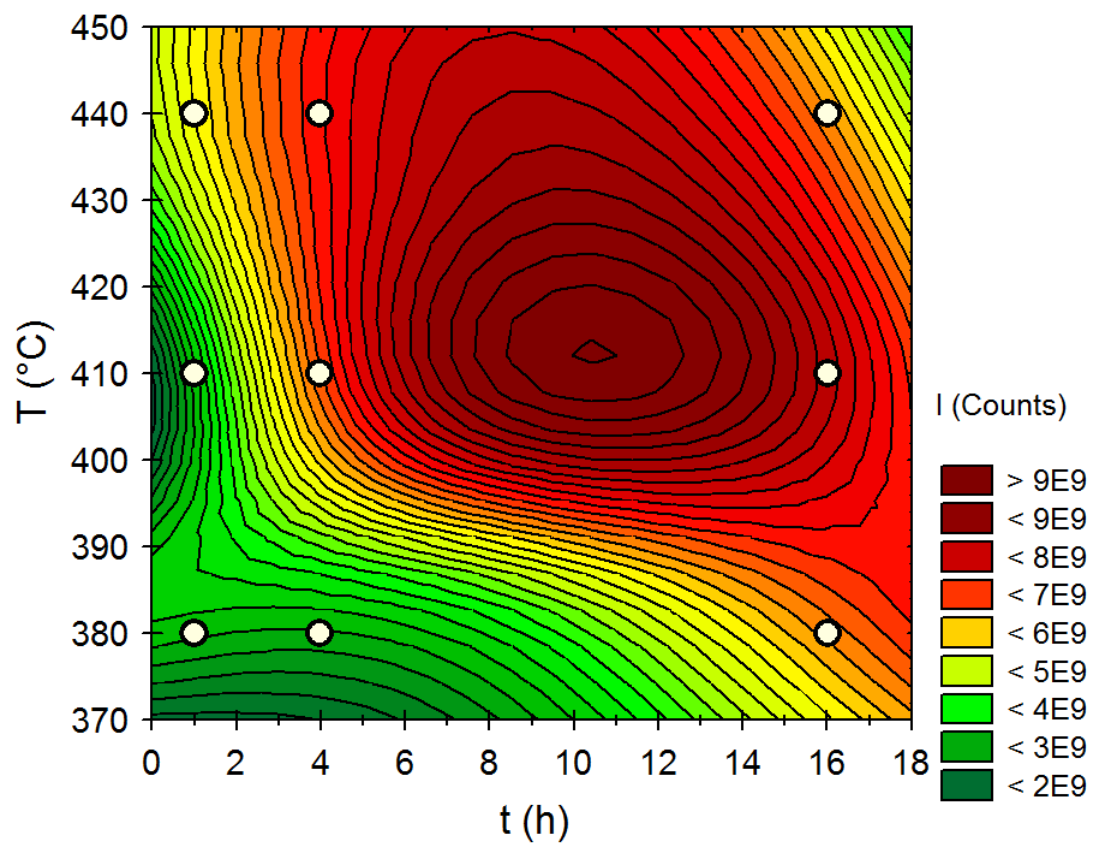
Fig. 1

Fig. 2

Fig. 3

Fig. 4.

Fig. 5.

Fig. 6.

Table 1.
Photoluminescence quantum yield (PLQY) measured at $\lambda_{exc-2}$=350 nm (emission in the 380–750 nm region) for some 1% samples. The annealing conditions are reported.

| SAMPLE | | | PLQY |
|---|---|---|---|
| 1% | as–exchanged | | **2%** |
| | 380°C | 4h | **17%** |
| | 410°C | 1h | **14%** |
| | | 4h | **8%** |
| | | 16h | **26%** |
| | 440°C | 1h | **13%** |