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## $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ nano-particles grown in porous silicon

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**Abstract.** We have succeeded to grow nano-crystalline  $\text{Zn}_2\text{SiO}_4 : \text{Mn}^{2+}$  particles by chemical impregnation of porous silicon layers and heat treatment. Two different classes of samples have been obtained: green luminescent samples at 525 nm and yellow luminescent ones at 575 nm. We identify the green luminescence as the conventional luminescence of the alpha phase of  $\text{Zn}_2\text{SiO}_4 : \text{Mn}^{2+}$ , however the yellow luminescence comes from the beta phase of  $\text{Zn}_2\text{SiO}_4 : \text{Mn}^{2+}$ . XRD peaks of the yellow luminescent samples show wide and weak peaks, indicating smaller particles, compared to green luminescent particles. We discuss about the conditions which result in either green or yellow luminescent samples.

### Introduction

Porous materials have been frequently used as a host to grow nano-structures. Porous silicon, having nanometer sized holes and with the ease of its formation is a good choice in this respect. The holes in the porous silicon layers allow impregnation of the layer with chemicals to grow other phases inside the layer or modify the properties of the layer. Impregnation of porous silicon with various dyes [1] is an example. On the other hand,  $\text{Zn}_2\text{SiO}_4 : \text{Mn}^{2+}$  is an important phosphor which is particularly used in plasma displays. Its powder form is usually synthesized by solid state reaction of the starting powders. It luminesces at green peaking at about 525 nm.

Here we report a new method to grow  $\text{Zn}_2\text{SiO}_4 : \text{Mn}^{2+}$  nano-particles into an oxidized porous silicon layer. This is a new concept in the impregnation of porous silicon, i.e. the growth of highly luminescent phosphor particles inside the porous layer. This involves the reaction of silicon walls with the impregnating chemicals, leading to a new phase inside the pores. This is also a new concept in phosphor applications, i.e. phosphor nano-particles embedded into a porous layer. In the following sections we report the details of experiment and results.

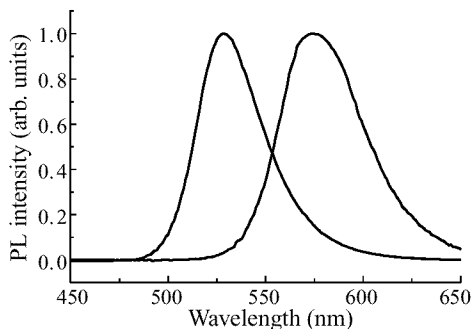
### 1. Experimental

Porous silicon layers were formed by the conventional electrochemical method. For most of the experiments,  $p^+$  type wafers were processed using 17.5 percent HF solution and 80 mA/cm<sup>2</sup> current density. This leads to meso-porous layers with 70 percent porosity and almost 10 nm pore size. The typical thickness of layers is 15 nm. Porous silicon samples were impregnated by immersing them into  $\text{Zn}(\text{NO}_3)_2 + x \text{Mn}(\text{NO}_3)_2$  solution for almost one hour.  $x$  is in the range of a few percent. Samples were then dried and put into the furnace for slow ramp heating up to 400°C followed by high temperature firing at 1050°C. This leads to the formation of Mn doped zinc silicate crystallites in a transparent matrix of oxidized porous silicon.

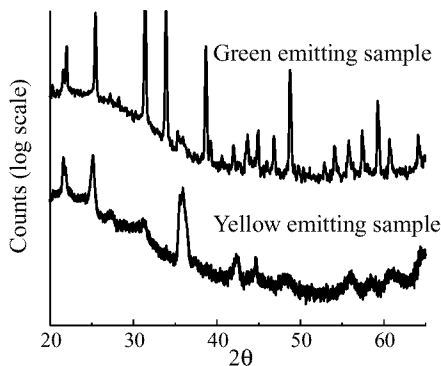
## 2. Results and discussion

With some variation in the details of the above conditions, both green and yellow luminescent samples can be obtained. These conditions are discussed later. Figure 1 shows the PL spectra for green and yellow luminescence at room temperature. The green luminescence is the conventional green of  $\text{Zn}_2\text{SiO}_4 : \text{Mn}^{2+}$  phosphor, occurring at about 525 nm. The yellow luminescence peaks at 575 nm, with a peak width of 54 nm compared to 38 nm in case of the green peak. The peaks are featureless, even at low temperature. Decreasing the temperature down to 10 K makes the peaks narrower, but the intensity does not increase more than 20 percent in both cases. For green samples, the peak intensity is up to 40 percent of the commercial  $\text{Zn}_2\text{SiO}_4 : \text{Mn}^{2+}$  phosphor, while this ratio is about 15 percent for yellow luminescence (by comparing the peak heights without instrument sensitivity correction).

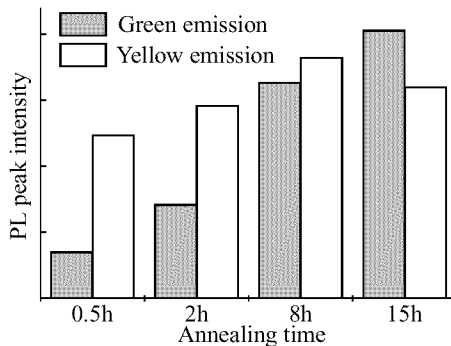
The PLE of both green and yellow are quite similar, with some blue shift in case of yellow one. This demonstrates that the origin of both luminescence is the Mn activator. More insight about the difference between green and yellow luminescent samples can be obtained by the XRD data. Figure 2 shows the XRD patterns for both kinds of samples. The pattern for the green sample corresponds exactly to the rhombohedral phase of  $\text{Zn}_2\text{SiO}_4$ , also known as  $\alpha - \text{Zn}_2\text{SiO}_4$ . There is no additional peak, indicating that no  $\text{ZnO}$ ,  $\text{MnO}_x$  or crystalline  $\text{SiO}_2$  is present. The relatively large size of particles explains the almost sharp diffraction peaks. From the peak width the size estimated to be about 200 nm. The XRD pattern for the yellow sample consists of weak and broad peaks, at positions different



**Fig. 1.** Normalized PL intensity for green and yellow luminescent samples.



**Fig. 2.** The XRD patterns of green and yellow luminescent samples. The green sample shows the peaks of  $\alpha - \text{Zn}_2\text{SiO}_4$ , while the yellow one resembles the  $\beta$  phase.



**Fig. 3.** Intensity of PL peaks of green and yellow luminescence for different annealing time at 1050°C.

from the rhombohedral  $Zn_2SiO_4$ . The pattern resembles that of  $\beta - Zn_2SiO_4$ , as reported by Taylor [2]. Like in case of the green sample, the pattern represents only one phase, demonstrating that the layer comprises  $\beta - Zn_2SiO_4$  particles embedded in an amorphous oxidized porous body. The size of the particles, calculated from the width of the diffraction peaks is typically 30 nm.

We found various conditions in which the yellow luminescence appears. An important factor is the period and temperature of annealing. Basically, shorter annealing time and lower temperature leads to yellow luminescence. Figure 3 shows the PL intensity of green and yellow peaks as the annealing time is increased. The annealing temperature is 1050°C. After 30 min annealing, the sample emits both yellow and green, with yellow peak being almost four times stronger than green. With increasing the annealing time, green/yellow ratio increases and after 15 h green is more intense than yellow. This effect suggests that the yellow emission comes from smaller particles and as the particle size increases with annealing time, more particles transform to green emission phase. XRD results also confirm that the size of yellow luminescent particles are smaller than green luminescent particles. This is supported by the fact that if we start with nano-porous silicon, instead of meso-porous one, with the same growth conditions, it usually leads to yellow luminescence. In nano-porous silicon the size of pores are about 3–4 nm and that makes the diffusion process and subsequently particle growth slower, leaving more of small yellow emitting particles.

## References

- [1] P. Li, Q. Li, Y. Ma and R. Fang, *J. Appl. Phys.* **80**, 490 (1996).
- [2] H. F. W. Taylor, *Am. Mineral.* **47**, 932 (1962).