STUDY ON THE INTEFFERENT FRINGE	NGHIÊN CỨU HIỆU ỨNG DỊCH CHUYỂN VÂN GIAO

SHIFT EFFECT OF THE PL SPECTRA IN NANOSTRUCTURED SILICON SAMPLE UNDER UV ILLUMINATION	THOA CỦA PHỔ PL TRONG MẪU SILIC CẤU TRÚC NANO CHIẾU XẠ UV
ABSTRACT We have observed interference effect in the photo luminescence (PL) spectra from the silicon nano-structured sample when the thickness of the emissive layer is much less compared with that of the SiO2 thin film lying between the silicon substrate and the Si/SiO2 multilayer nanofilm. Typically, the silicon film thickness is about 1 μm, and the Si/SiO2 multilayer nanofilm thickness ranges from 200 to 400 nm. However the thickness of the emissive layer is reduced for several times due to different effects, such as the surface PL enhancement. The location and the effective thickness of the luminescence layer can be calculated based on the position and modulation depth of the interference fringes. When illuminated with UV beam in the vacuum, the PL intensity from the sample is increased considerably. This effect was tested under different conditions and the results show that the thermal increasing effect does not play any role in this PL	TÓM TẮT Chúng tôi quan sát hiệu ứng giao thoa trong phổ quang phát quang (PL) của mẫu silic cấu trúc nano khi chiều dày của lớp phát xạ nhỏ hơn nhiều so với độ dày của màng mỏng SiO2 nằm giữa đế silic và màng mỏng nano đa lớp Si/SiO2. Thông thường, chiều dày màng silic khoảng 1 μm, và độ dày màng nano đa lớp Si/SiO2 nằm trong khoảng từ 200 đến 400 nm. Tuy nhiên, độ dày của lớp phát xạ giảm vài lần do các hiệu ứng khác nhau, chẳng hạn như tăng cường PL bề mặt. Vị trí và chiều dày hiệu dụng của lớp phát quang có thể tính dựa vào vị trí và chiều sâu điều biến của các vân giao thoa. Dưới tác dụng của chùm UV trong môi trường chân không, cường độ PL của mẫu tăng đáng kể. Hiệu ứng này được kiểm tra trong các điều kiện khác nhau và các kết quả cho thấy rằng sự tăng nhiệt độ không đóng vai trò quan trọng trong quá trình tăng cường PL này.

enhancement. Furthermore, when illuminated continuously by UV beam, the distances between fringes reduce, and the modulation depth increases. The origin of this effect is still under study. We continue also the study of the influence of the sample structures and annealing temperature on the increase of PL efficiency and interference spectrum structures.

Hơn nữa, khi chiếu xạ liên tục bằng chùm UV, khoảng cách giữa các vân giảm, và chiều sâu điều biến tăng. Nguồn gốc của hiệu ứng này vẫn đang được nghiên cứu. Chúng tôi cũng tiếp tục nghiên cứu ảnh hưởng của cấu trúc mẫu và nhiệt độ nung đến sự tăng hiệu suất PL và cấu trúc phổ giao thoa.

INTRODUCTION

The influence of the interference effect on the shape of the luminescence spectra was known, and one theoretical model was proposed in the work of Holm and co-workers [1]. The conditions by which the interference effect modifies the shape of the luminescence spectrum is that the thickness of the light emitting layers must be much smaller than that of the main film, therefore, in most studies, the interference effect was not observed, although they appear in the transmission and reflection spectra.

In some works on the nano structured silicon film, the interference effect of the PL spectra was observed, for example in the PL spectrum of the carbon doped SiO2 film of Seo [2], we can see some

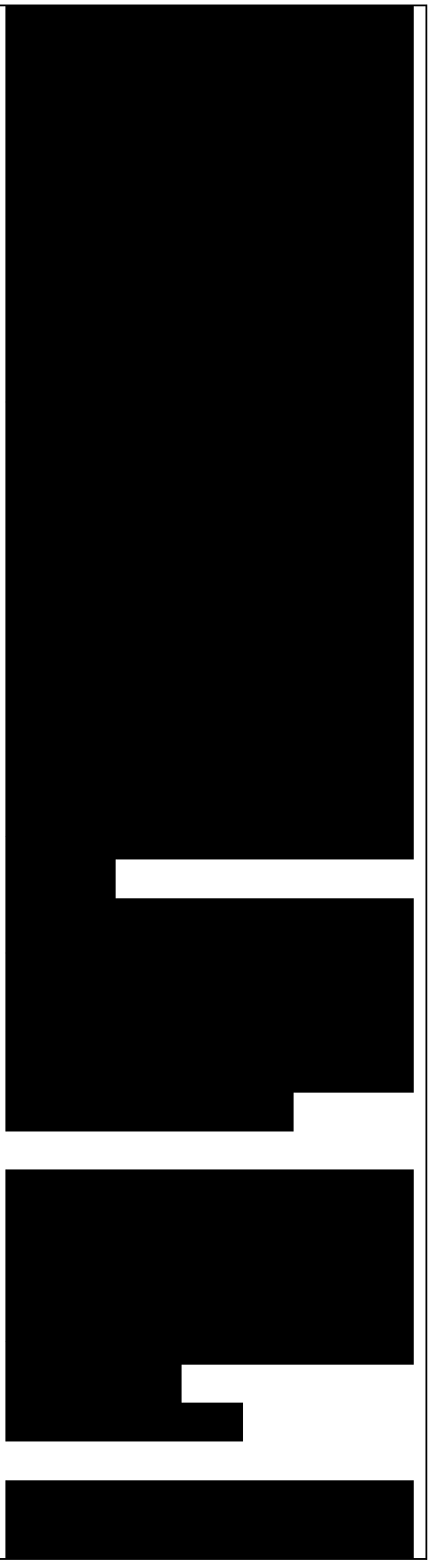
interference fringes. However, the author didn't pay attention to these phenomena and there was no explanation to it. In our previous work, we have presented the observation of the interference effect in the PL spectra in the nano structured silicon sample, produced by co-sputtering method. In this work, we will present in more detail the dependence of the interference fringe contrast on the illuminated laser energy in various conditions. In addition, in the Si/SiO2 multi layer samples, the efficiency of the PL enhancement as well as the increase of fringe contrast happen in the longer wavelength side.

Fig. 1. Structure of S278 sample with the 200 nm sol-gel and 3 nm silicon films. The sample was annealed in the nitrogen atmosphere at different temperatures, from 400 oC to 1100 oC.

The origin of these phenomena is not yet clear, but we will give some explanations and discuss about the validity of these suppositions.

EXPERIMENTS

We have designed two types of sample with different



structures for these studies. The structure of the sample labeled S278 is illustrated in the Fig.1, consisting of the silicon substrate, on which 1 □m film was deposited to form an insulation layer. Then, a film of about 200 nm-thicknesses was deposited by sol-gel method. On top of the solgel layer, a silicon layer of several nanometer thicknesses was made by sputtering deposition. The details of the fabrication technology were presented in the previous works. Our idea is that the nanopores in the solgel film can be the locations for the silicon atoms, diffused from the top layer into it, and then form the nano crystals when annealed at high temperature.

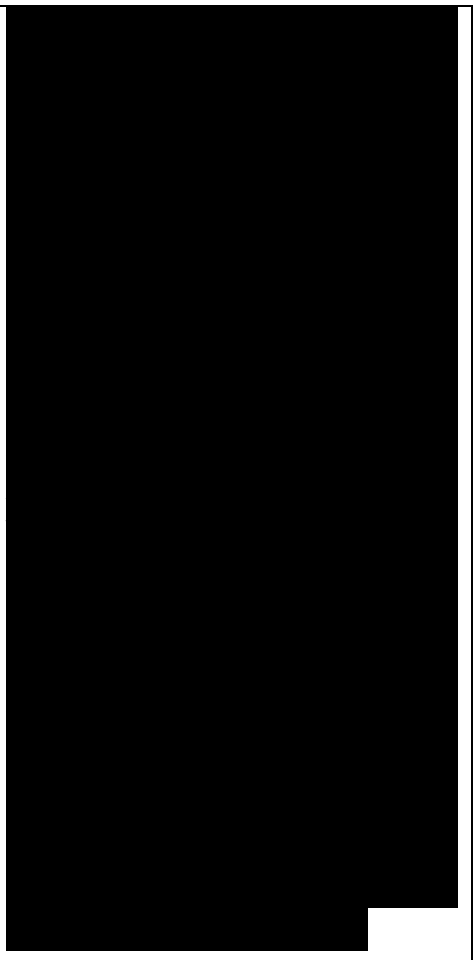


Fig. 2. Structure of S278 sample with 50 layers of Si/SiO2 films with the thickness 1 nm and 2 nm respectively. The sample was annealed in the nitrogen atmosphere at different temperatures from 400 oC to 1100 oC.

The second type of sample, labeled S270 has a little difference (Fig. 2). Instead of the solgel and thin silicon films are 50 layers of Si/SiO2 films with the thickness of 1 nm and 2 nm. When annealed at high temperature, we think

that silicon atoms will adhere each with others and form the nano crystals. All these samples were fabricated in ITIMS laboratory.

Fig. 3 shows the AFM image of the S278 sample surface annealed at 1000o C in the nitrogen atmosphere. In order to investigate the influence of the interference effect and UV illumination on the structure and the intensity of the PL spectra, we have measured the PL in different conditions. The PL sample was excited by different wavelengths of the Cd-He laser (325 and 442 nm) The excitation intensity can be changed using different neutral filter, placed between the laser and the sample. The sample was mounted on the cold finger of the cryostat with variable temperature, ranging from 10 oK to 300 oK.

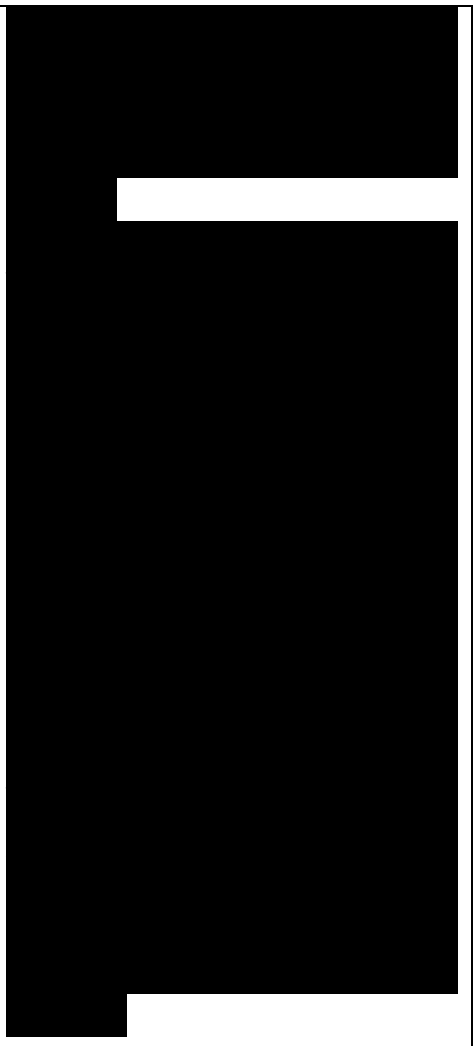


Fig. 3. AFM image of the 278 image surface after thermal annealing. Each division is equivalent to 15 nm, showing that the roughness of the surface is around 1-2 nm.

At room temperature, we can change the gas environment surrounding the sample, such as air, nitrogen or argon. The pressure can vary from 10-4 Torr to atmospheric pressure. The laser beam was focused on the sample by 40 cm focal

length quartz lens. The luminescent signal was collected by a 20 cm focal length lens, mounted on the optical axis, which is perpendicular to the sample surface. The aperture of the lens can be change using a small diaphragm. When the collection solid angle is small, the interference fringe contrast is large, but the signal intensity is decreased. The light signal is focused on a fiber optical bundle, and then transmitted to the entrance slit of the 32 cm Microspec spectrometer. Using 150 g/mm grating and cooled CCD, we can record all the spectrum range from 350 nm to 850 nm in one click. Due to the continuous recording option, we have recorded 30 spectra during 30 minute in illuminating the sample by the laser beam, in order to observe the impact of the 325 nm laser beam on the intensity and structure of the PL spectra.

RESULTS AND DISCUSSION

When investigate the PL spectra in the vacuum, excited by 325 nm line, we have received the spectra having the intensity increasing with the illumination time. The PL enhancement is not uniform at different wavelength,

depending on the sample types. Fig. 4 shows the 3D plot of the PL spectra depending on the illumination time using 325 nm line. The laser power is 20 mW, focused into a spot of 0.5 mm, giving a density of about 10W/cm2. We see that after the continuous exposure to laser beam during 30 minutes (in 10-3 Torr vacuum); the PL intensity has increased to 300%, and is not yet saturated. This is a surprised phenomenon, since in general, when illuminate the sample with a laser beam, the PL intensity has a tendency to be quenched. A rare case of the enhancement of PL intensity was reported by Shir and co-worker [4], when illuminated the argon laser beam to the porous silicon. However, after illuminating during 30 minutes, the PL intensity increased only 30% and had saturation.

The second particularity observed in Fig. 4 is that the depth of the interference fringes increase with the illumination time. As we have mentioned in the introduction section, although the interference effect is easily observable in the transmission and reflection spectra of the film, having the thickness

comparable with the excitation wavelength, but is rarely observable in the luminescence spectra.

In the previous reports, the depths of the interference fringes were only around 20%, smaller than that observed in our non- exposed – to- UV sample. It is understandable if we consider the Holm model [1], since in our structure, there is a SiO2 insulation layer of 1 µm thick, while the thickness of luminescent layer is only150 nm. When illuminate by laser beam, the interference modulation depth can increase until 70 – 80 %, or by other word, only the interference maxima increase, while the minima remain with the same intensities. These phenomena can lead us to an illusion, that we have observed 6 different luminescence bands.

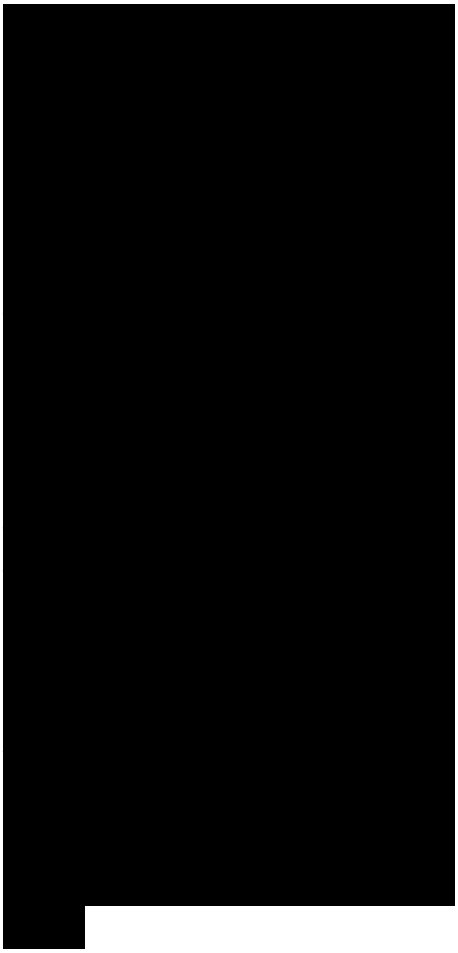
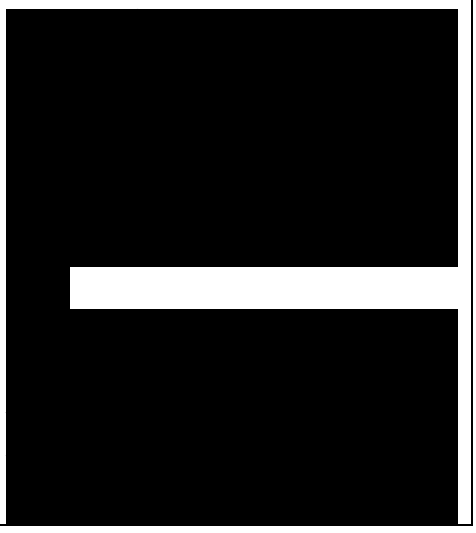


Fig. 4. PL spectra of S278 sample under UV illumination in vacuum. Each spectrum was recorded with 1.5 minute delay interval. Some bands are not yet saturated.



Based on the simulated calculation, we can conclude that, phenomenological, the PL enhancement effect under laser radiation is not uniform;

the enhancement efficiency near the surface is much larger than in the bulk. This effect results in the increase of the luminescence centers near the surface and leading to the increase of the fringe depths.

In order to understand the mechanism leading to the PL enhancement effect under laser illumination, we have carried out the measurements under different conditions. The 442 nm laser beam with 5 times power more (100 mW) was used to illuminated during 30 minutes in vacuum, then the PL intensities before and after the expose were compared. The results showed that there is no special effect, although the thermal energy absorbed with 442 nm was 5 times larger than that with 325 nm (absorption mainly by silicon substrate). We have also heated the sample to 200 oC in the vacuum in order to make the evaporation of the adsorbed substance on the surface, however, no change of the PL spectra was observed. In summary, in order to observe the effect of PL enhancement, the energy of the illumination beam must be greater than 3 eV.

We have noticed that in the S278 series, the PL intensity was recorded for the sample

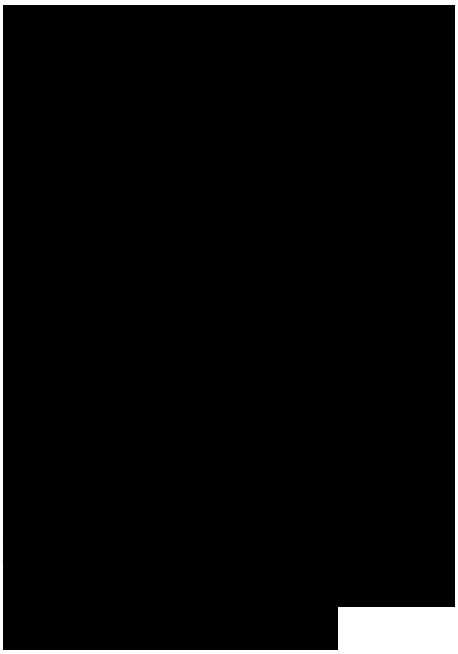
annealed at temperature 600 oC. The PL spectrum is green yellow overlapped broad bands, attributed to the recombination of NBO centers (NBOC-Non Bridging Oxygen Center). When the annealing temperature is greater than 1050 oC, only the emission band originates from silicon nanocrystals (750 nm) remains. Under the UV illumination in vacuum, the PL intensity increases to 300-4005 again, and its magnitude is comparable with the value when annealed at 600 oC, but the peak intensity was shifted to the IR side. The structure of the spectrum is modified due to the influence of the interference effect.

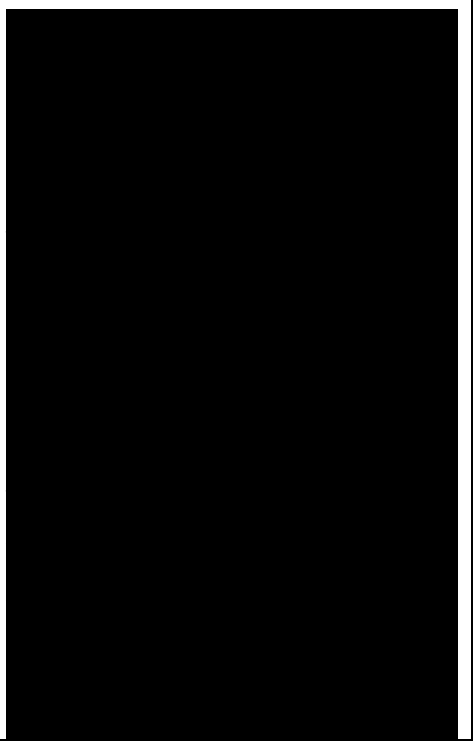
In the second series of samples, labeled S270, consisting of Si/SiO2 multilayer, the PL enhancement and interference fringe modification effects are more pronounced. Fig. 5 shows the PL spectra of the S270 sample, annealed in the nitrogen environment at 1000 oC during 1 hour, exposed to 5 mW UV beam during 1 minute and 96 minutes. It is worth to mention that the annealing temperature 1000o C is not high enough to form silicon nanocrystals in the SiO2 matrix; hence the PL

spectra before the UV illumination give us a blue band, with rather regularly distributed interference fringes.

Under UV illumination in vacuum, two phenomena appeared. First, the PL intensity increased considerably in a broad band ranging from 360 to 900 nm. In the region from 600 nm to 900 nm, at the beginning, the PL intensity was almost zero, but after the exposure to laser beam, a strong PL band appeared and increased continuously with the exposure time. The PL intensity in this region was increased about 50 times and continues to broaden to the IR side.

The second phenomena were that the depth of the interference fringes increased with the exposure time, proving that the PL enhancement happens mainly near the surface. We have not yet investigated the stability of these luminescence centers, produced by this method. In the rich Si/SiO2 film produced by different methods (PE CVD, Co-Sputtering, Solgel), in general, we can observe white-blue emission band when the annealing temperature is bellow 1100 [2,



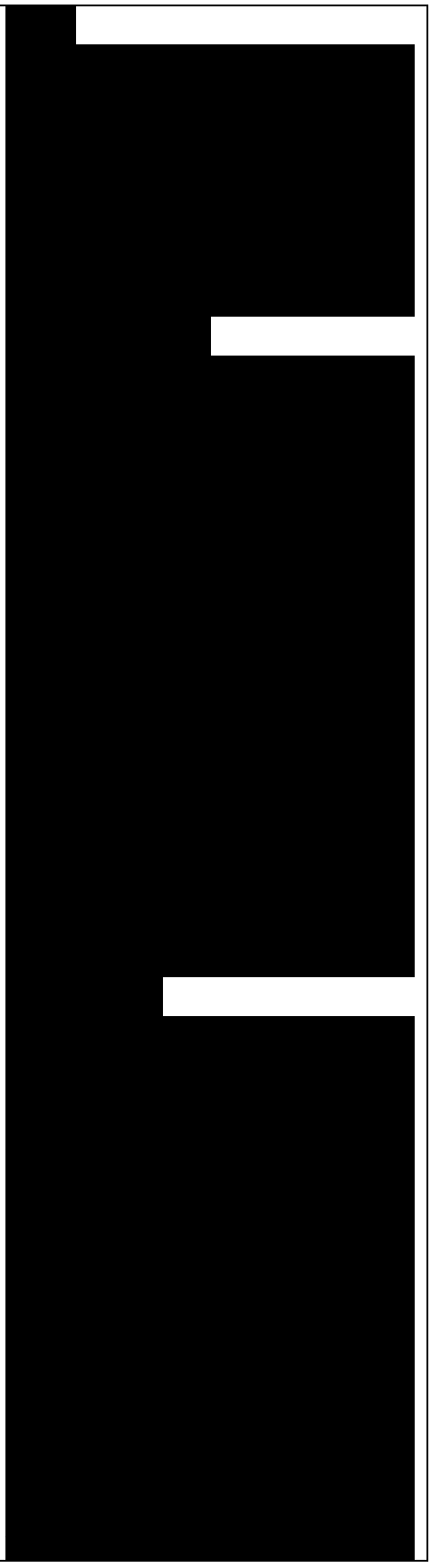


3, 4].

Fig. 5. PL spectra of S270 sample under UV illumination in vacuum, with exposure time 1 minute and 96 minutes. The laser power is 5 mW, equivalent to 20 minute exposure time using 20 mW in Fig. 4.

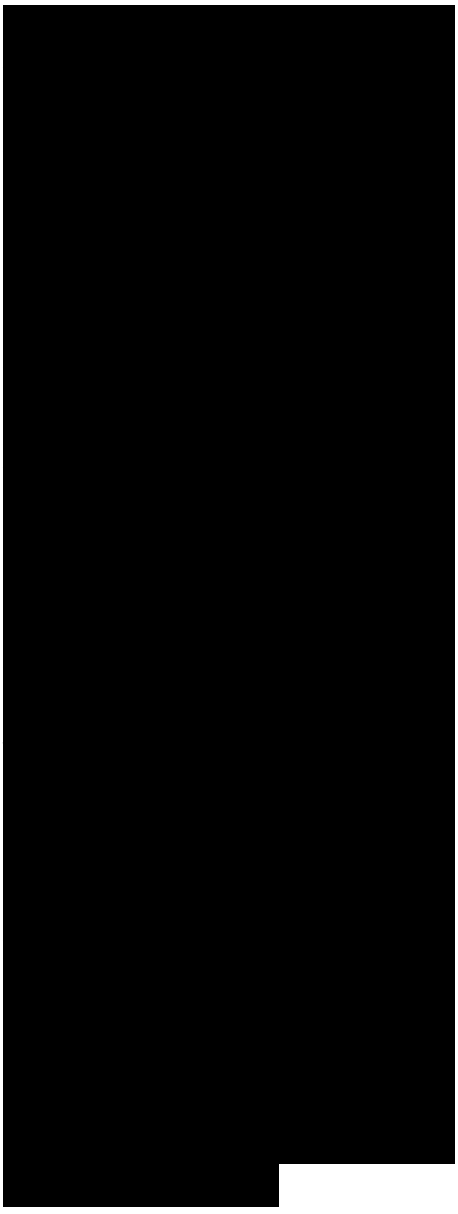
When the annealing temperature is greater than 1100 oC, the white-blue band almost disappears, instead, the red or infra-red appears. In the previous studies, such a large emission band ranging from 350 nm to 900 nm was not observed, included the porous silicon PL. Therefore, by using the UV laser annealing in vacuum, we can fabricate a material with strong white light emission. Furthermore, the light centers are located near the surface, which reduce the PL re-absorption effect.

The PL spectra shown in the Fig. 4 and Fig. 5 with the alternative maxima and minima, but it do not mean that the integral intensities of the minima are less compared with that of the maxima. When we record the PL spectra under different angle, at the wavelength where the intensity was minimal can be now the maximum. When we plot the PL intensity as the function of the energy, the



distances between the peaks are always the same. The interference effect permits us to determine the location and the distribution of the luminescence layers. The calculation can be done using the Holm' model [1] and the information from the absorption coefficient of the film at 325 nm.

The mechanism of PL enhancement is not yet clear, but we can propose a model based on the following arguments. For the PL band related to the nanosilicon crystals or porous silicon, having in general the peaks at 700-800 nm, some authors supposed that its intensity depend not only on the size of the nanocrystals, but also on the its surface states [4]. There are a lot of dangling bonds on the surface of silicon nanocrystals, forming the non radiative recombination centers, which quench the PL intensity. In our opinion, under laser illumination, a catalytic process took place and the separation of water molecule giving hydrogen and oxygen atoms. Therefore, the passivation of the dangling bond by the hydrogen atoms on the surface will reduce the non radiative recombination and increase the PL intensity.



In vacuum, the oxygen atoms evaporate from the surface quickly, so there is a small probability of oxidation of hydrogen atoms. That can be the reason why the PL enhancement is more pronounced at the surface.

When we illuminate the sample in the air, the oxidation process is considerable and the density of dangling bonds increase again, which reduce the PL intensity.

In the S278 samples, the blue band at 550 nm (which is not yet accepted as POR center [5] or silicon nano cluster [6]) and the red band at 650 nm (which is attributed to NBOC) have also the similar PL enhancement effect. So in our opinion, they have the same origin, relating to very small silicon clusters, rather than the defects relating to the oxygen vacancy of the matrix.

CONCLUSION

The method of producing interference film permit us to determine the position of the luminescence centers, as well as the thickness of this light layer, in the silicon rich silicon dioxide nano films. Under laser illumination in vacuum, we have increased the PL intensity by some orders, especially under the sample surface. For S720 sample, the

IR emission band, which is in general attributed to the exciton recombination in the silicon nanocrystals, was produced. For the first time, such a broad emission band ranging from 350 nm to 900 nm was produced by laser annealing method in vacuum.