Visible photoluminescence of porous silicon covered with an HfON dielectric layer*

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Abstract: With HfON filling the holes in porous silicon (PS), films with improved photoluminescence (PL) at room temperature were prepared. A strong blue peak at 425 nm and a red peak at 690 nm were observed in PL spectra. It is believed that the quantum-limited effect (QLE) and the polycrystalline structure of HfON is responsible for the observed PL peaks. The stoichiometric proportion of N/O in the HfON layer has also a great influence on the intensity of blue light emission. Finally, the temperature quenching effect was observed to be greatly weakened for the incorporation of HfON.

Key words: hafnium oxynitride; dielectrics; diffusion; luminescence; porosity

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1. Introduction

Recently, high demand for light-emission diodes (LEDs) has occurred due to the development of display and communication technology in the ultralarge scale integrated circuit (ULSI) field. Thus, many LED materials, such as GaAs, InGaN and AlGaN have received intensive attention[1, 2]. However, due to the lattice mismatch problem these materials are hard to integrate into cheap and universal ULSI devices. Meanwhile, they are generally fabricated from expensive single crystals, and thus the applications of them are greatly limited. Serving as an LED material, PS has two obvious advantages compared with other materials. One is that LEDs made from PS are easily integrated into chips and can transact logical operation and result translation with high speed. The other advantage is that the emission wavelength can be adjusted by the eroding process of PS. However, there are still many problems before PS can be put into applications, such as its low light emission efficiency due to the indirect energy gap of bulk Si, unstable emission characteristics due to the H-terminated surface and its sensitivity to the fabrication method[3]. Among these, the main issue is the efficiency of light radiation, which is not strong enough for utilization. In this paper, HfON was deposited onto the surface of PS by filling into the holes using low power sputtering[4]. A loomed visible blue peak can be observed for the HfON covered PS sample after high temperature annealing. To the best of our knowledge, such a strong PL intensity has not been reported before. Since Hf-based dielectrics, including HfON, are considered promising materials to replace the traditional SiO_2 gate of CMOS transistors in ULSI devices, the integration of HfON with poly Si is very attractive for photoelectric applications[5−7].

2. Experimental details

Polished n type (100) single crystal Si with a resistivity of 5 Ω·cm was firstly cut into several rectangular parts with areas of 1 cm^2, then ethanol, acetone and deionized water were used for cleaning. Afterwards, the anode electrochemical corrosion method was used to fabricate PS samples. The corrosion liquid is a mixture of HF and ethanol in 1 : 1 volume ratio, and the current density was controlled at 25 mA/cm^2. After 8 min corrosion, the samples were cleaned in deionized water, followed by natural drying in air. After the PS treatment, HfON was deposited onto the surface of PS in N_2/O_2 ambient using a pure Hf target (99.99% purity). The distance between target and substrate was kept constant at 8.0 cm during deposition. The base pressure of the sputtering chamber before deposition was 3.5×10^{-4} Pa and the working pressure was kept at −0.3 Pa. The deposition power density was kept at 50 W/cm^2 and the film thickness was about 500 nm. Due to the dense character of sputtering films, holes on the surface of PS could be sufficiently filled. A lower power was used to reduce the surface damage. Afterwards, samples were eroded in HF: ethanol solution again in order to expose the PS surface for further luminescence investigations. Finally, to investigate the effect of annealing on the PL characteristics, samples were annealed in vacuum ($\sim 10^{-5}$ Torr) for 30 min at different temperatures.

The film thickness was measured by an ellipsometer. Fourier transform infrared (FTIR) spectra were recorded by a Bomem MB-100 spectrometer using the KBr wafer technique. Room temperature PL spectra were measured using a spectrofluorophotometer (RF-540) by using the 325 nm line of a He–Cd laser as an excitation source.

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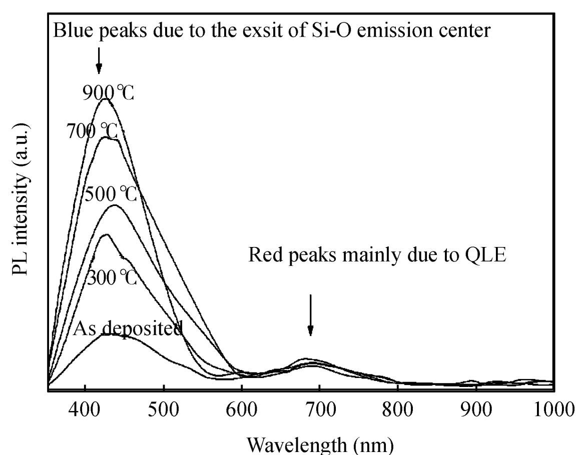

Fig. 1. PL spectra for the HfON covered PS films. The samples were annealed in vacuum conditions at 500, 700 and 900 °C, respectively. All PL peaks were excited with a 325 nm He–Cd laser.

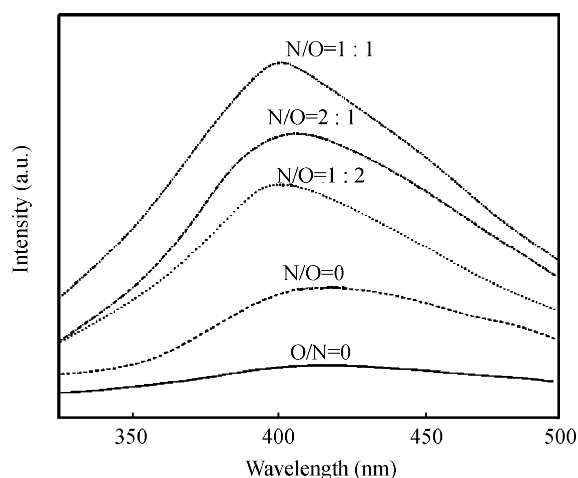

Fig. 2. Evolution of the intensity of PL under different N/O ratios in HfON layer. The intensity of the blue peak originally increases and then decreases as the N/O ratio increases.

3. Results and discussion

According to the earlier literature, there are two obvious PL bands for PS[11, 12]: One is at 600–700 nm due to the surface state or quantum-limited effect, and the other is in the blue region, 440–450 nm, which is attributed to an Si–O emission center near the surface. Figure 1 is the PL spectra of the HfON-covered PS films annealed in vacuum at 300, 500, 700 and 900 °C respectively. It can be seen that there are also two obvious PL peaks at about 425 and 690 nm. The peak at 690 nm is consistent with the previously-reported red PL peak as mentioned above, while the peak at 425 nm is somewhat lower than the generally reported value. The blue emission at 425 nm was loomed with the naked eye after high-temperature annealing (≥ 700 °C). To the best of our knowledge, PS samples seldom have such strong emission intensities[13−15]. HfON should not be the direct reason for these peaks, since there has been no related report on it up to now. Using the previous reports, one can deduce that the red peak in the PL spectra is the intrinsic emission bands of PS, and the blue peak at 425 nm should be strongly related to the HfON incorporation.

The effect of the variation of N/O ratio on PL spectra was investigated as shown in Fig. 2. It can be confirmed from this measurement that the enhancement of the blue peak at 425 nm is strongly related to the HfON incorporation. One can see that the position of the emission peak is only slightly related to the change of N concentration, but the intensity of peaks is a sensitive case: it originally increases and then decreases as N/O increases. The maximum intensity occurs when the N/O value reaches about 1 : 1. This requires further investigation for a full understanding of the initial increase and subsequent decrease of the emission intensity as N/O ratio increases. A cursory explanation attributes this fact to the diffusion efficiency of O in the HfON layer, which can be modulated by N concentration. Greater N concentration adsorbs more oxygen for oxidation due to the existence of the Hf–N metastable phase, further leading to the reduction of Si–O emission centers

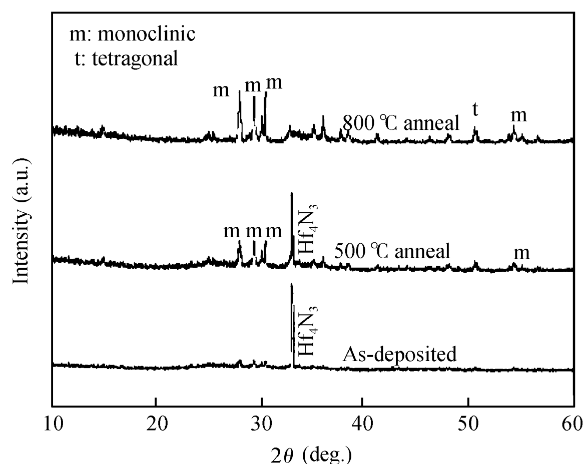

Fig. 3. Typical X-ray diffraction patterns of HfON annealed at different temperatures in vacuum.

at the interface. On the other hand, reducing N too much will lead to more defects in unstoichiometric HfON during excessive oxygen transport. The defect sites in HfON will result in non-directional movement/scattering of photo-generated carriers, reducing carrier combinations at emission centers correspondingly. Figure 3 shows XRD patterns of the HfON (N/O = 1 : 2) films as the annealing temperature varies. One can find HfN phase in our sample from XRD spectra. The as-deposited films exhibited a relatively intense diffraction peak at 33°, which denotes the HfN phase. The peak at 30.5° is attributed to the β-$Hf_7O_8N_4$ phase. Meanwhile, there are other monoclinic and tetragonal phases in the spectra related to different HfO_2 crystal phases. From the XRD spectra, it can be seen that as the annealing temperature increases, the intensity of the Hf_4N_3 diffraction peak decreases whereas the intensity of other HfON or HfO_2 diffraction peaks increases. This is consistent with the above-mentioned oxidation in HfON bulk. Moreover, more new peaks appear for the 800 °C annealed sample due to crystallization. This polycrystalline structure may also lead to new emission centers due to the quantum lim-

ited effect.

The polycrystalline structure of HfON may lead to the formation of inner electrical fields with spontaneous polarization due to the localized carrier concentration in separate crystals. The photo-generated electrons and holes will move directionally through the polycrystalline boundaries due to the attraction of the static electrical field. Thus, the diffusion of carriers is greatly limited when recombination is enhanced at the interface region, where there are sufficient Si–O emission centers due to oxidation. It is known that the diffusion of carriers into point defects is generally responsible for non-radiative recombination. Even in high-quality PS, this non-radiative recombination is predominant. This directional transport of charge effectively confines the diffusion of carriers. However, it will also lead to carrier scattering due to the existence of distorted conductive HfN crystal points and defects introduced due to the unstoichiometric N/O ratio. Therefore, a suitable N/O ratio and annealing for the reduction of defects is necessary. Moreover, because high temperatures accelerate O diffusion, Si–O emission centers are greatly increased, and thus blue emission is enhanced as annealing temperature increases. Additionally, the HfON layer can passivate the H-terminated surface of PS with oxidation. Since the diffusion of O in the HfON layer is gradual[8], and can be adjusted by changing the N concentration, sharp oxidation can be effectively avoided. Thus the combination of holes, which are reported as non-radiative centers on the PS surface[9, 10], is greatly limited. This is a cursory explanation for the observed fact; further investigation is under consideration.

Annealing is helpful for the process of replacing the H-terminated surface with an O-terminated surface. To investigate the change of chemical bonds in samples, a FTIR measurement was applied as shown in Fig. 4. It can be found that peaks related to SiH_x species with different Si–H modes (stretching 2100 cm^{-1}, wagging 660 cm^{-1} and scissor 910 cm^{-1}) were greatly weakened as annealing temperature increased. Most of them vanished after 500 °C annealing. However, the integral intensity of the IR-peaks (peaks at 880 and 1100 cm^{-1}) related to the Si–O bond shows an increase with increasing annealing temperature. From the FTIR spectra, it can be concluded that SiH_x species are efficiently lustrated by annealing. Annealing can improve the property of the HfON/PS interface and reduce SiH_x species to restrain red emission. However, the red peak did not vanished when the Si–H emission center disappeared, which is assumed to be due to the quantum-limited effect (QLE) of nanocrystals in HfON and Si[16, 17]. According to previous reports[18, 19], the crystallization temperature is generally at 500–700 °C for HfON films. The band-to-band emission at nanocrystals seems to also compensate the lack of red emission centers. Thus, it can be concluded that photo-generation of carriers not only occurs in Si crystals, but can also take place in the HfON layer. In this way, carriers for recombination are greatly increased. HfON

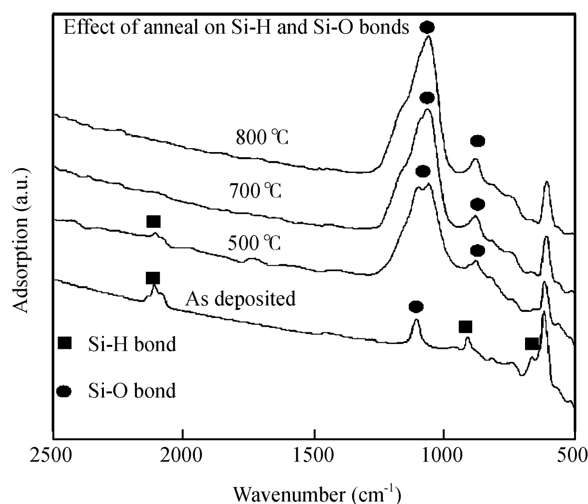

Fig. 4. Evolutions of FTIR spectra as annealing temperature increases. Annealing was performed in vacuum conditions for 30 min. Peaks related to SiH_x species with different Si–H modes (stretching 2100 cm^{-1}, wagging 660 cm^{-1} and scissor 910 cm^{-1}) were greatly weakened as annealing temperature increased. Si–O bonds (peaks at 880 and 1100 cm^{-1}) increase as annealing temperature increases.

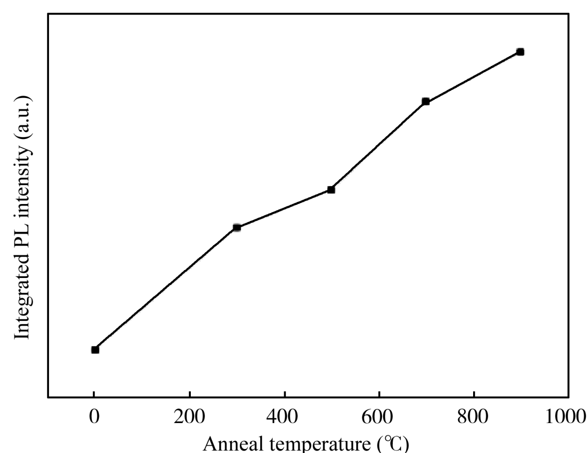

Fig. 5. Integrated PL intensity as a function of the annealing temperature in vacuum for 30 min. No temperature quenching effect was observed in the range of our annealing temperatures.

may not only confine carriers but also contribute more carriers for recombination.

The annealing temperature dependence of the integrated PL intensity was shown in Fig. 5. In most light-emission systems[20, 21], PL quenches very strongly with increasing annealing temperature, making heat treatment problematic in luminescence device applications. However, in our films it was observed that the PL intensity increased as annealing temperature increased to even 900 °C. As required, therefore, the device is partly free from the disturbance of the temperature quenching effect in the annealing process. Strong temperature quenching of PL is generally a result of the strong temperature dependence of competing non-radiative routes—the band-to-band transition is relatively temperature-independent[22]. In our case, spatial localization of the radiative carrier population decouples it from any non-radiative recombination occurring

elsewhere, thus eliminating luminescence quenching.

4. Conclusion

In summary, HfON was deposited by low power sputtering into the holes of PS in order to enhance the PL intensity of PS. In PL spectra, the blue emission (325 nm) increases as annealing temperature increasing while the red emission (690 nm) remains constant. Together with the results of FTIR measurement, it is concluded that there are two dominant emission centers: Si–O and nanocrystals in films responsible for the blue and red peaks respectively. HfON not only confines the diffusion of carriers due to its polarized field but also contributes more carriers after heat treatment for recombination. Additionally, it is also observed that the temperature quenching effect is greatly weakened for the incorporation of the HfON layer. It is believed that the incorporation of HfON in an optical cavity not only benefits PS, but is also suitable for other materials, especially indirect materials or Si alloy.

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