

# Effect of Lattice Mismatch on Luminescence of ZnO/ Si Hetero-Structure \*

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**Abstract:** The photoluminescence (PL) and Raman spectra of undoped ZnO films deposited directly on Si substrate (sample A), on Si substrate through a SiC buffer layer (sample B), and on a ZnO crystal wafer (sample C) are investigated. There are emission peaks centered at 3.18eV (ultraviolet, UV) and 2.38eV (green) in these samples. Comparing the Raman spectra and the variation of the PL peak intensities with annealing atmosphere, we conclude that the luminescence of the samples is related to the tensile strain in the ZnO film due to the lattice mismatch between the film and the substrate. In particular, the tensile strain reduces the formation energy of  $O_{Zn}$  antisite oxygen defects, which generate the green emission center. After annealing in oxygen-rich atmosphere, many  $O_{Zn}$  defects are generated. Thus, the intensity of green emission in ZnO/Si hetero-structure materials increases due to tensile strain in ZnO films.

**Key words:** ZnO/Si hetero-structure; luminescence; lattice mismatch; biaxial tensile strain

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## 1 Introduction

ZnO is of interest because of its potential applications in blue and UV light-emitting devices and in optoelectronics. In order to fabricate practical ZnO-based devices, it is very important to get high-quality ZnO films and understand the luminescence mechanism of ZnO films. Silicon wafers are widely used as substrate because of their low cost and additional advantages in optoelectronic integration. However, there is a large strain at the interface of the epitaxial film and the substrate due to the large lattice mismatch between ZnO and Si, which induces defects in the film that deteriorate the film quality when it relaxes. Therefore, it is important to study the strain and the subsequent defects in epitaxial ZnO films. Generally, there are two major emission bands in the room-temperature photoluminescence (PL) spectrum of ZnO films. A dominant ultraviolet band centered at 380nm is attributed to exciton recombination, and a weak one centered at about

525nm, called the "green band", is thought to be related to intrinsic defects in undoped ZnO films. Different authors attribute the green emission to different intrinsic defects in ZnO film, such as singly ionized oxygen vacancy ( $V_O^{\cdot}$ ), zinc vacancy ( $V_{Zn}$ ), and interstitial zinc ( $Zn_i$ )<sup>[1-6]</sup>. We verified in our previous work<sup>[7]</sup> that the green emission center of the ZnO film deposited on Si substrate is related to  $O_{Zn}$  antisite oxygen defects. However, there is an important question that was not answered in that paper. The formation energy of  $O_{Zn}$  is very high (about 4.6eV), prompting the question of whether  $O_{Zn}$  defects can be generated in ZnO films. In this paper, we present an investigation of the formation mechanism of  $O_{Zn}$  based on recent experimental results and theoretical analysis.

## 2 Experiment

In our experiments, three kinds of samples are investigated. The first is ZnO film directly deposited on Si(111) substrate (sample A), the sec-

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ond is ZnO film deposited on Si substrate through a SiC buffer layer (sample B), and the third is single-crystal ZnO (sample C). The former two samples were prepared in a special high-temperature MOCVD system, which has two connected reaction chambers, one for growing SiC film and the other for ZnO. The details of the growth process were reported in the previous paper<sup>[8]</sup>. After deposition, the samples were annealed for 1h in a range of temperature 700 ~ 900 in air and oxygen, respectively. The Raman spectra were obtained with a 514.5nm wavelength Ar<sup>+</sup> laser on a LABRAM-HR confocal laser micro-Raman spectrometer. The PL spectra were measured using a 325nm wavelength He-Cd laser for excitation. The sample was also characterized with X-ray diffraction (XRD) measured by a Philips X'Pert Pro double crystal diffractometer.

### 3 Results

Figure 1 shows the XRD patterns of samples A and B as-prepared, and the insets are the respective rocking curves of the ZnO (002) plane. It is clear that both samples have only ZnO (002) and (004) peaks, but their rocking curves have significantly different profiles. The full width at half maximum (FWHM) of the rocking curve for sample A is about 7°, while that for sample B is reduced to only 1.2°. This result demonstrates that the crystal quality of the epitaxial ZnO film has been greatly improved by using the SiC buffer layer.

Figure 2 shows the Raman spectra with a range of wave number from 350 to 600cm<sup>-1</sup> of the samples A, B, and C, respectively. All of them were measured under the same conditions. According to group theory, ZnO has eight sets of optical phonon modes at  $\Gamma$  point of the Brillouin zone,  $A_1(TO, LO) + 2B_1 + E_1(TO, LO) + 2E_2$ . Both  $B_1$  and  $E_2$  consist of two modes of low and high frequency. Of the eight modes, only  $A_1, E_1, E_2$  are Raman active, while  $B_1$  is inactive. In the backscattering geometry in our experiment, the incident light is parallel to the  $c$ -axis of the ZnO sample. Therefore, only  $E_2$  and  $A_1(LO)$  are allowed according to the Raman selection rules<sup>[9]</sup>. Since the  $E_2(\text{high})$  mode represents the band characteristic of wurtzite ZnO, the intensity of

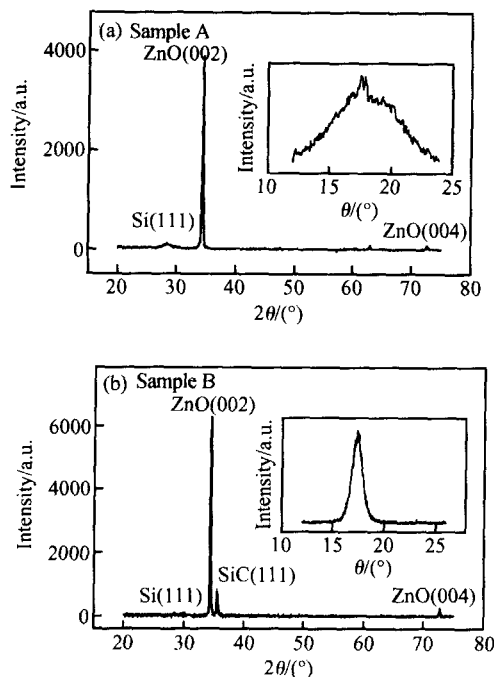


Fig. 1 XRD patterns of samples A (a) and B (b). The inset is the X-ray rocking curve of the ZnO (002) plane.

this peak is much stronger than that of the others in ambient conditions<sup>[10]</sup>, so that the  $A_1(LO)$  peak is usually unobservable, as shown in this Raman spectrum. For sample C, the only sharp and strong peak is the  $E_2(\text{high})$  peak at 437.1cm<sup>-1</sup>. The position of this peak shifts to a lower frequency — about 1.9 and 0.9cm<sup>-1</sup> for sample A and sample B, respectively.

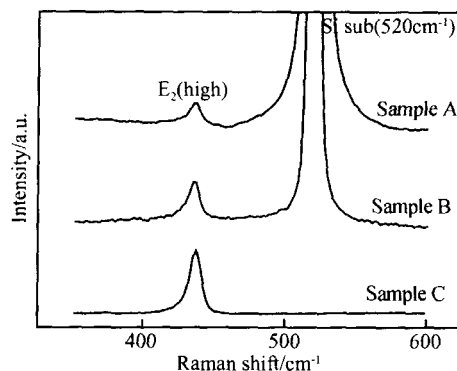


Fig. 2 Raman spectra of three samples

According to the calculation and experimental results of Decremps et al.<sup>[9]</sup>, the Raman shift of ZnO is closely related to the strain in the film. They pointed out that in the  $c$ -axis oriented ZnO

epilayers ,the  $E_2$  (high) mode will shift to a higher frequency as a result of compressive stress and to a lower frequency as a result of tensile strain. The correlation between the Raman shift and the stress can be simply expressed as  $(\text{cm}^{-1}) = 4.4 (\text{GPa})$ ; i. e. there is a 0.227 GPa net strain in the film for every  $1\text{cm}^{-1}$  shift. According to this formula ,samples A and B ,for which the red-shifts are 1.9 and  $0.9\text{cm}^{-1}$  ,have tensile strains of 0.43 and 0.20GPa, respectively. Table 1 lists the detailed data of the Raman spectra.

Table 1 Raman spectra results of the  $E_2$  (high) mode of the samples

Sample	Peak position of $E_2$ (high) / $\text{cm}^{-1}$	$E_2$ (high) frequency shift / $\text{cm}^{-1}$	Tensile strain / GPa
C	437.1	/	/
A	435.2	- 1.9	0.43
B	436.2	- 0.9	0.20

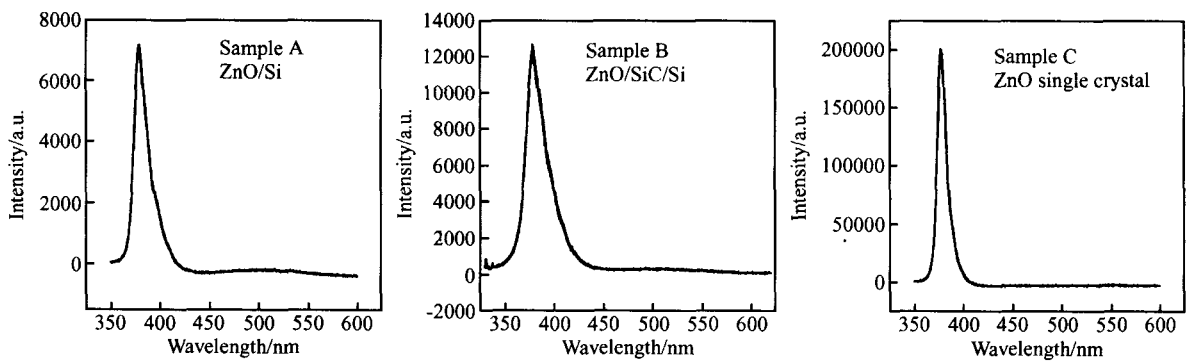


Fig. 3 PL spectra of the three samples at room temperature

It is thought that the ultraviolet emission in ZnO is attributed to the recombination of excitons. Generally, better crystal quality helps reduce exciton scattering, thereby increasing the exciton emission probability. Therefore, the single crystal ZnO has the strongest and ZnO/ Si has the weakest UV emission.

As for the green emission, our previous work demonstrated that it is closely related to the antisite oxygen defects  $O_{Zn}^{17}$ . However, there is still a problem that was not solved in that paper. The radius of  $O^{2-}$ , 0.14nm, is much larger than that of  $Zn^{2+}$ , 0.074nm, and the electro-negativity of oxygen, 3.5, is also much larger than that of zinc, 1.65. Thus,  $O_{Zn}$  has too high a formation energy to be generated in ZnO single crystal. Therefore, it is necessary to study the formation mechanism of

These results show that the SiC buffer layer can effectively modulate the tensile strain in ZnO film, because the SiC buffer layer reduces the mismatch between ZnO and Si. It is also conformed to XRD.

Figure 3 shows the PL spectra at room temperature of samples A, B, and C excited by a 325nm He-Cd laser. There are two obvious emission bands in the spectra, a dominant ultraviolet emission band centered at 380nm and a wide and weak green emission band centered at 520nm. In Fig.3, Sample A has the lowest UV peak and the highest green peak. Sample C has the strongest UV intensity and an almost unobservable green emission peak. It is evident from Fig.3 that the intensity of the UV and green emission is strongly related to the tensile strain in the films. The larger the tensile strain in the films is, the lower the intensity of the UV emission becomes and the stronger the intensity of the green emission becomes.

$O_{Zn}$  defects in ZnO films.

From the experimental results here, we believe that the formation of  $O_{Zn}$  is the result of tensile strain in films. The fact that tensile strain existing in the ZnO film indicates that there is lattice-enlarged deformation in the ZnO film, even though this deformation might be somewhat modulated by a SiC buffer layer. Generally, tensile strain in films raises the system energy. In order to reduce the system energy to make the system more stable, the tensile strain must be relaxed by generating defects, each of which is composed of an ion with a larger radius substituted for a smaller one. Thus, antisite oxygen defects  $O_{Zn}$  can form easily. That means that tensile strain reduces the formation energy of  $O_{Zn}$ . As larger tensile strain causes a higher concentration of  $O_{Zn}$  defects, the

green emission intensity increases when the tensile strain increases (see Fig. 3).

In order to test this deduction, the effect of annealing on the photoluminescence of samples A (ZnO/Si) and B (ZnO/SiC/Si) was investigated as shown in Fig. 4. Figure 4 (a) compares the PL spectra of samples A and B annealed in air at 850 °C for 1h. Comparing with Fig. 3, it is clear that not only the UV intensities of both samples A and B increase due to the improved crystal quality of the ZnO film by annealing, but also the green emission intensities increase due to the relaxation of tensile strain in the film, and sample B has a stronger UV intensity and a weaker green intensity than sample A has. This means the larger tensile strain in ZnO films could generate more intrinsic defects, which generate the green emission center, even though the crystal quality of the ZnO film was improved by annealing. Figure 4 (b), in which the y axis is displayed on a logarithmic scale in order to project the variation of the green emission intensity, shows the PL spectra of sample B annealed at 700 °C for 1h in air and oxygen, respectively. In this figure, it is observed that the UV intensity decreases and the green emission intensity increases with the increase of the oxygen partial pressure in annealing. This indicates that an oxygen atmosphere generates more intrinsic defects, thereby intensifying the green emission center, and subsequently attenuating the UV emission.

It is known that annealing relaxes strain and improves the crystal quality of ZnO films, so that exciton scattering is reduced and the UV intensity increases. However, Figure 4 (a) shows that the green emission intensity is also enhanced after annealing, and the larger the tensile strain is in the ZnO film, the greater the increase of the green emission intensity is. These phenomena indicate that the number of intrinsic defects, which lead to green emission in undoped ZnO films, is increased by annealing, and a larger tensile strain in ZnO films is more favorable for generating these defects in the strain-relax process. Furthermore, the higher the oxygen partial pressure is in annealing, the stronger the green emission becomes for a sample, as shown in Fig. 4 (b). This variation is similar to that of  $O_{Zn}$  defects, which lead to the green emission center that we reported before<sup>[7]</sup>.

The above phenomena demonstrate that the  $O_{Zn}$  defect generates the green emission center, and the formation mechanism of  $O_{Zn}$  in the ZnO film deposited on Si substrate is related to tensile strain in the films.

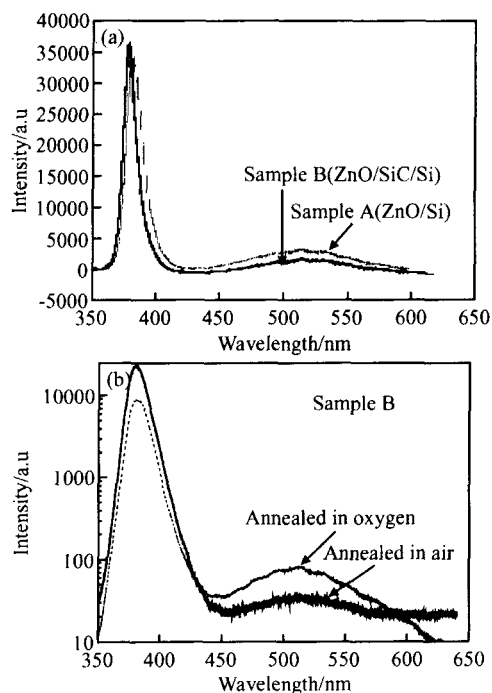


Fig. 4 (a) PL spectra of samples A and B annealed in air for 1h at 850 °C; (b) PL spectra of sample B annealed at 700 °C for 1h in air and oxygen, respectively

We have also noticed that Ashkenov et al.<sup>[11]</sup> used RBS and IRSE measurements to study ZnO films deposited on sapphire substrates. They pointed out that the vacancy defects in their samples were mainly responsible for the optical behaviors. It is thought that there is compressive stress in their films because the lattice constant of the films is larger than that of the substrates. Their experiment provides further evidence that the  $O_{Zn}$  defects in the ZnO film deposited on Si substrate which are responsible for the green emission center are formed mainly due to the tensile strain in the films.

## 4 Conclusion

In summary, the XRD, Raman, and PL spectra of ZnO/Si (sample A), ZnO/SiC/Si (sample B), and the single crystal ZnO (sample C) have been measured and investigated. It is observed

that there are tensile strains in the epitaxial ZnO films of both samples A and B due to the mismatch between ZnO and Si, while a SiC buffer layer modulates and reduces this tensile strain. This tensile strain in ZnO films greatly influences the photoluminescence properties, including the ultraviolet and green emission of the ZnO epitaxial films. Moreover, the larger the tensile strain is in the ZnO film, the weaker the intensity of the UV emission is, and the stronger the intensity of the green emission is. After annealing in air and oxygen, not only are the UV intensities of both samples A and B increased due to the improved crystal quality of ZnO film by annealing, but the green emission intensities are also increased due to the relaxation of the tensile strain in the film. Sample A, with larger tensile strain, has stronger green emission and weaker UV emission. In particular, the green emission intensity increases rapidly and UV emission attenuates when the annealing atmosphere is changed from air to pure oxygen. These phenomena indicate that the intrinsic defect, which is responsible for green emission in undoped ZnO film, is closely related to tensile strain in ZnO films and that a higher oxygen partial pressure in annealing is more favorable for generating this defect. The above results not only demonstrate our suggestion reported in Ref. [7] that the  $O_{Zn}$  defects are responsible for the green emission center in undoped ZnO film deposited on Si substrate, but also explain the formation mechanism of  $O_{Zn}$ . Because tensile strain in films generally raises the system energy, it must be relaxed by

generating  $O_{Zn}$  defects, which consist of an ion with larger radius substituted for a smaller one. Therefore,  $O_{Zn}$  antisite oxygen defects can be formed with the help of tensile strain.

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## 应力对 ZnO/Si 异质结构的光致发光的影响\*

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**摘要:** 研究了 ZnO 薄膜中应力对发光的影响. 实验样品为 ZnO 体单晶、在 Si 基片上直接生长的 ZnO 薄膜以及通过 SiC 过渡层在 Si 基片上生长的 ZnO 薄膜. 测量了这三种样品的 X 射线衍射图形、喇曼光谱和光致发光光谱. 由 X 射线衍射图形可以看出, 由于 SiC 过渡层缓解了 ZnO 与 Si 之间的晶格失配, 使得通过 SiC 过渡层在 Si 上生长的 ZnO 薄膜的结晶质量好于直接在 Si 上生长的 ZnO 薄膜的质量. 进一步通过喇曼谱测量发现, 与 ZnO 体单晶相比, 直接在 Si 上生长的 ZnO 薄膜的  $E_2(\text{high})$  峰红移  $1.9\text{cm}^{-1}$ , 根据喇曼谱峰位移与应力的关系可以推出薄膜中存在  $0.4\text{GPa}$  的张应力; 而通过 SiC 过渡层在 Si 上生长的 ZnO 薄膜的  $E_2(\text{high})$  峰红移  $0.9\text{cm}^{-1}$ , 对应着  $0.2\text{GPa}$  的张应力. 对照 X 射线衍射图形的结果可以看出, 薄膜中张应力的大小与薄膜的结晶质量密切相关, 表明张应力来源于外延层和基片间的晶格失配, 晶格失配越大, 外延层中产生的张应力越大. 有无 SiC 过渡层的两种薄膜样品的 PL 光谱中都存在紫外和绿光两种谱带, 随样品热处理时氧气分压增加, 两种样品都出现绿光增强的相似的变化规律, 但有 SiC 过渡层的样品的变化幅度较小. 这一结果说明, 绿色发光中心与薄膜的质量, 也就是与薄膜中存在的张应力大小有关. 在以往研究中得出的非故意掺杂 ZnO 薄膜的绿色发光中心来源于氧反位缺陷 ( $\text{O}_{\text{zn}}$ ), 文中研究的结果正好可以解释氧反位缺陷形成的原因. 由于薄膜中存在张应力, 使得样品的能量升高, 其结果必然会产生缺陷来释放张应力, 以便降低系统能量. 而氧离子半径大于锌离子半径, 氧替位锌有利于释放张应力, 也就是说, 在存在张应力的情况下,  $\text{O}_{\text{zn}}$  的形成能降低. 这一结果进一步证明 Si 上生长的 ZnO 薄膜中的绿色发光中心与氧反位缺陷有关.

**关键词:** ZnO/Si 异质结构; 光致发光; 晶格失配; 双轴张应力

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