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Investigations on structural, morphological, optical and spectroscopy properties of ZnO films

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Abstract: *ZnO films on Si (100) and morphous silica substrate have been successfully deposited using RF magnetron sputtering. Different annealing temperature is used after deposition of films. X-ray diffrction (XRD) study reveals that grown films have hexagonal wurtzite structure and preferebly orientation along (002) direction. Surface morphology of the grown films have been studied using scaning electron microscopy (SEM). UV visible transmittance spectra shows that films grown on amorphous silica has high transmittance. Photoluminescence study carried out to study the intrinsic defects of the films.*

Key Words: *Structural study ; optical study ; thin film.*

1. INTRODUCTION:

Zinc oxide films have attracted broad attention of research community due to excellent properties exhibited which is useful for various applications such as, Solar Cells [1], Photo detectors[2], light emitting diodes [3], gas sensors [4], surface acoustic devices [5] Optoelectronic devices [6] etc. ZnO films have been prepared by various deposition techniques such as Pulsed Laser Deposition (PLD), Sol-Gel, Sputtering, Plasma enhanced chemical vapour deposition (PECVD), Metal organic chemical vapour deposition (MOCVD), Molecular Beam Epitaxy (MBE) and Atomic Layer Deposition (ALD) [9-12]. Among these techniques, Sputtering has advantage of producing a uniform and highly oriented film even at low processing temperature. Taking account of these things in this communication reported thin films have been grown at room temperature.

Mostly, the researchers have grown the ZnO films on sapphire substrate due to its good lattice matching with ZnO film in the c-axis direction. But, when comes to the practical applications of the ZnO films, it is desirable to grow ZnO films on Si substrate, since it is cheaper and available in large size and easy to use in advanced Si electronics. Moreover, the thermal expansion co-efficient value of Si is also very close to that of ZnO. However, the only drawback of the Si substrate is the large lattice mismatch between the ZnO film and Si substrate. Moreover, it is also difficult to grow ZnO films on Si substrate without having formation of Silica layer at the interface of film and substrate. Because, the formation enthalpy of ZnO (-350.5 kJ/mol) is much less in magnitude with respect to SiO_2 (-910.7 kJ/mol). Therefore, the formation of SiO_2 is more favourable and likely to happen first. This formation of SiO_2 layer can be minimized if somehow one can control oxygen around the Si substrate during the initial stage of growth of film. This can be possible by eliminating oxygen during the growth of films. In this report, we have grown ZnO films on Si (100) substrate using RF magnetron Sputtering in the ultra high vacuum to minimize the formation of SiO_2 layer at the film-substrate interface. Then, instead of giving Oxygen partial pressure at the time of deposition, later we annealed the film in air.

2. MATERIALS AND METHODS:

ZnO thin films were deposited on Si (1 0 0) substrate using RF magnetron Sputtering in an ultra high vacuum. The ZnO target was purchased commercially with >99.99% purity with rectangular shape. Prior to the growth of ZnO films, the target was pre-sputtered for 20 minutes to remove any surface contamination. The sputtering chamber was evacuated to a base pressure of 6 X 10^{-7} Torr. ZnO films was deposited at a fixed RF power of 80 Watts. A working pressure of 5 X 10^{-3} Torr was maintained using only argon (99.99%) gas. The crystalline structure was determined, using a powder X-ray Diffractometer (Panalytical Pro). The surface morphology and cross-sectional images of the films

was been taken using Scanning Electron Microscope. Optical transmittance spectra were taken in the ultraviolet (UV)-Visible range. Photo Luminescence (PL) measurements were been taken using LS 55 luminescence spectrometer (by perkin elmer) equipped with deuterium and halogen lamps as source for UV and visible source, respectively. The excitation wavelength used was 330 nm.

3. RESULTS AND DISCUSSION:

Fig. 1 shows the XRD pattern of ZnO film deposited on Si substrate and then annealed in air at three different temperatures 500C, 700C and 900C for 1 hrs. During the annealing heating and cooling rate was kept constant at 1C/min. All the ZnO films grown on Si showed a Hexagonal wurtzite structure and preferably oriented in a (002) direction. The peak intensity of (002) reflection increased considerably with increase in annealing temperature. It suggests that increase in annealing temperature results in more oriented structure. In the as deposited film, the bragg angle 2θ of the ZnO (002) reflection is 33.82 (for bulk ZnO is 34.44). The 2θ value for the films annealed at 500C, 700C and 900C are 34.51, 34.52 and 34.53, respectively. The bragg peak shifts toward the higher angle nearer to its bulk value. This observed shift is mainly due to the lattice strain present in the film. The lattice strain δ along the (002) direction in the film has been calculated using the following formula:

$\delta_{(002)} = d_{bulk} - d_{film} / d_{bulk} \times 100$

where d_{bulk} is the lattice spacing of bulk while d_{film} is the lattice spacing for film.

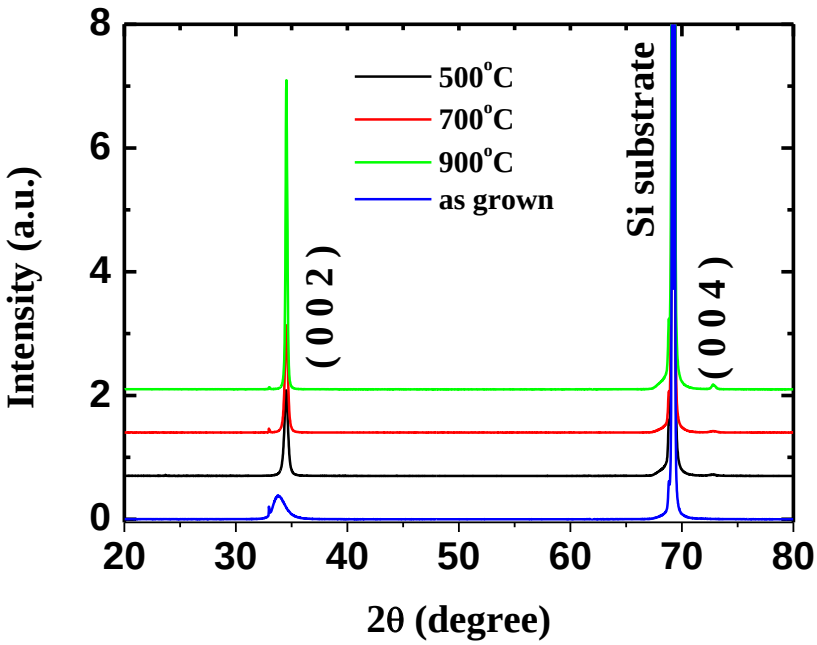


Figure 1: XRD pattern of ZnO films grown on Si substrate and annealed at three different annealing temperature 500C, 700C and 900C for 1 Hrs.

The d_{bulk} (2.604 A) is obtained from taking the XRD of ZnO powder. The calculated strain δ (002) for the ZnO films are -1.81%, 0.19%, 0.23% and 0.23% for the as deposited ZnO film & annealed at 500C, 700C and 900C, respectively. It can be seen that, as deposited films possess high strain in the lattice but after annealing the film at 500C in air the strain decreases quit a lot. But, beyond the 500C up to 900C it doesn't make any significance change. Thus, it can be understood that as grown films possess high strain which can be devoted to the large lattice mismatch between bulk ZnO and the Si substrate. While after annealing, shifting of 2θ peak at higher bragg angle suggests the decrease in strain along the c-axis direction.

The Full width at half maximum (FWHM) value calculated from (002) peak was 1.36 degree before annealing and it decreases with increasing annealing temperature and ultimately becomes 0.14 degree for the films annealed at 900C which indicates an increase of crystallite size means improvement in the crystallinity with annealing temperature.

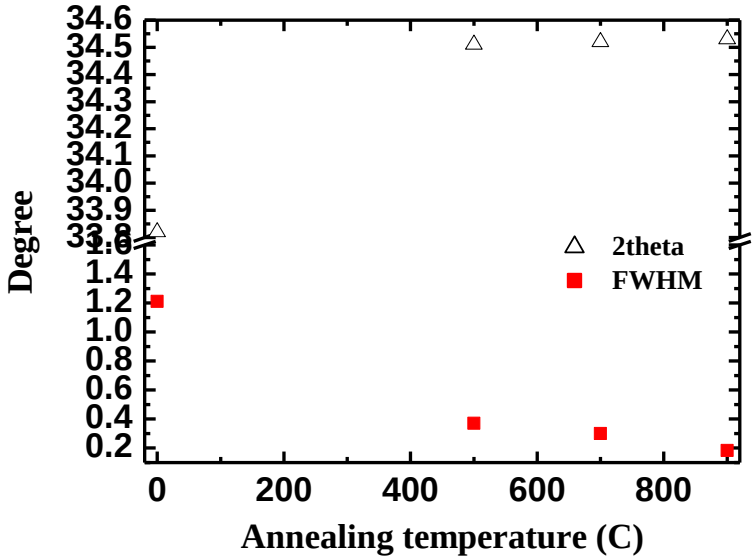


Fig.2 Annealing temperature dependent FWHM and 2θ position of (002) peak of ZnO films on Si substrate.

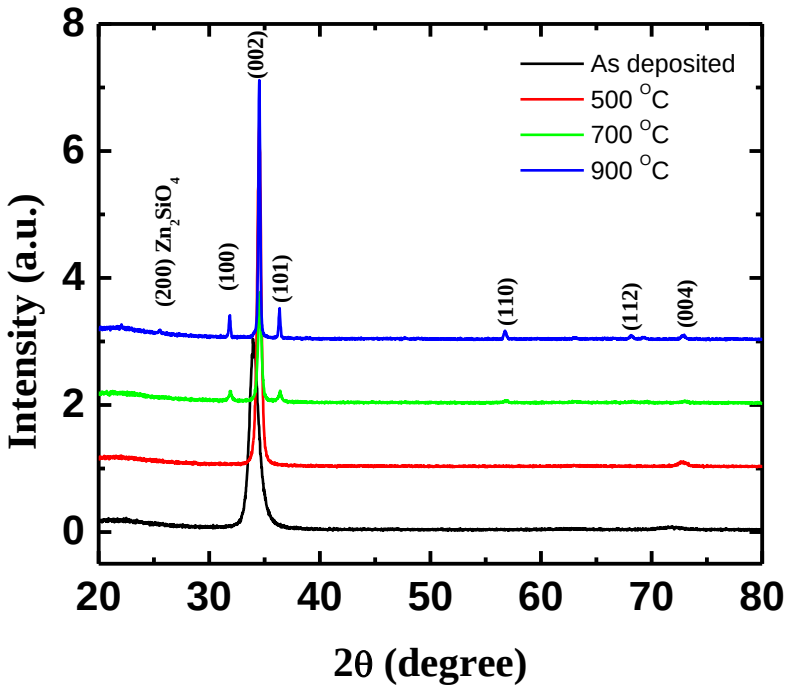
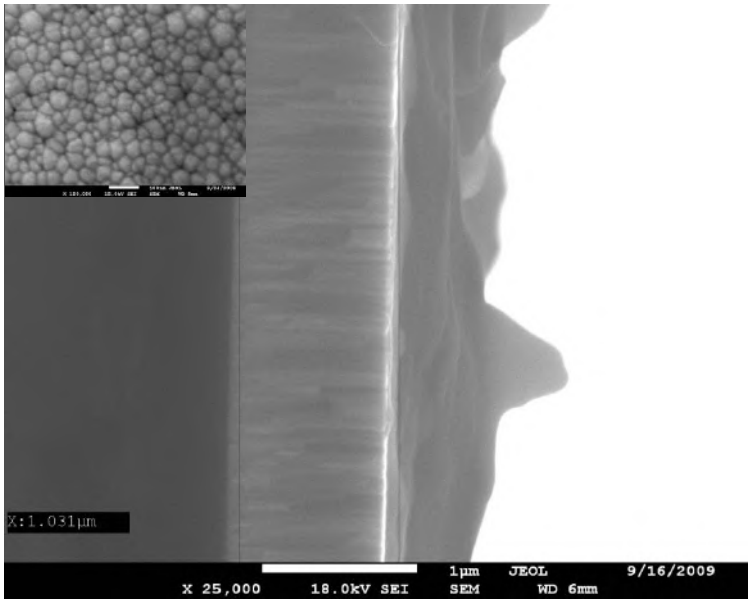


Figure 3: XRD pattern of ZnO thin film grown on amorphous silica substrate using RF Sputtering at 80W power.

Fig. 3 shows the XRD pattern of ZnO films deposited on amorphous silica substrate and then thermal treatment was given same as for the film grown on Si substrate. All the ZnO films grown showed a Hexagonal wurtzite structure having preferable orientation of ZnO, along (002) direction. The peak intensity of (002) reflection increased considerably after annealing up to 900C. Other important thing is that, 700C and 900C annealed films losses its orientation at this point and becomes randomly oriented so other plane reflections start to appear in the XRD pattern. It seems that at and above 700C, the films unit cells starts to reorient itself and in order to do this film loses its orientation

in preferred direction and becomes randomly oriented in case of amorphous silica substrate but same behaviour has not been observed in case of Si substrate. It can be assumed that, this randomly orientation in the films at high temperature might have origin in the substrate effect.

For the films annealed at 900C, additional peak is observed which matched with Zn_2SiO_4 tetragonal phase (JCPDS data). This phase may be grown at interface of the film and substrate since >700C is sufficient high temperature that amorphous silica can easily react with ZnO present at the interface. Though, the amount of Zn_2SiO_4 present in the film is very low.In order to check the interdiffusion of films with substrate, we have taken cross-sectional SEM images for the films grown on Si substrate. The SEM imges taken from top and cross section are shown in Fig. 4.



Figire 4: a) SEM image of ZnO films on Si substrate annealed at 500C.

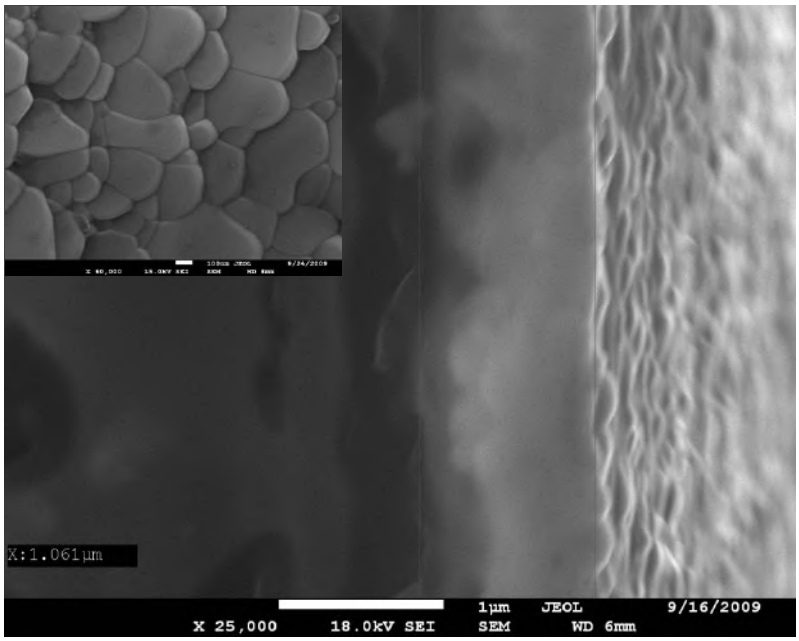


Figure 4: b) SEM image of ZnO films on Si substrate annealed at 900C.

It can be seen from all the figures that, at 500C the interface of film and substrate is smooth and there is no any diffusion between film and substrate. While for the films annealed at 900C, the interface of film and substrate seems no smoother. Moreover, the drastic increase in grain size is observed for the film at 900C. From the inset of fig. 4 b) it can be seen that surface of film is constituted by flat plates of ZnO. These are seems to be separated and superimposed. It may be possible that all individual platelets are preferably oriented but not the all.

Table – 1 Annealing temperature dependent 2θ peak position, inter planar spacing "d", FWHM and lattice strain δ calculated from (002) peak for the ZnO film grown on Si and Quartz substrate.

Sr.No.	Annealing temp.	2θ (degree)		d (A)		FWHM		δ (in%)	
		Si	Quartz	Si	Quartz	Si	Quartz	Si	Quartz
1	0	33.82	33.96	2.651	2.640	1.210	0.939	-1.805	-1.382
2	500C	34.51	34.53	2.599	2.598	0.370	0.396	0.192	0.230
3	700C	34.52	34.59	2.598	2.593	0.300	0.357	0.230	0.422
4	900C	34.53	34.53	2.598	2.598	0.184	0.194	0.230	0.230

Table-1 shows the annealing temperature dependent 2θ peak position, inter planar spacing "d", FWHM and lattice strain δ calculated from (002) peak for the ZnO film grown on Si and amorphous silica substrate. It can be revealed from the table that, with the increase in annealing temperature the trend of 2θ, d, FWHM and δ is almost same. So, the annealing temperature effect on all these parameters is same for both the substrates. But, the lattice strain along (002) direction it seems quite less for the films on Quartz substrate as compared to films on Si substrate, for instance, the δ value for as grown films are -1.80% and -1.38% for the Si and amorphous silica substrate, respectively. The same things can be deduced from 2θ peak position and d value for the films grown on both substrates. Because 2θ and d values seems to be near compared with pure ZnO powder for the films grown on amorphous silica substrates.

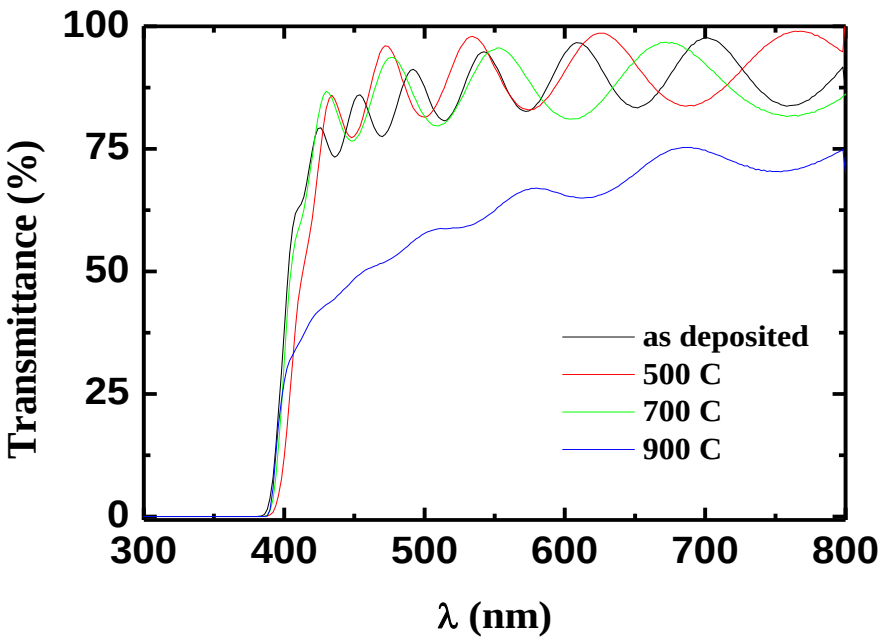


Figure 5: UV- Visible Transmittance spectra for ZnO film on amorphous silica.

The optical measurements were done on the ZnO films grown on amorphous silica. The optical transmittance spectra of the as deposited and annealed ZnO films are shown in fig. 5, where transmitted intensity is plotted as a function of wavelength. All the films showed the transmittance above 80% in the visible region except for the film annealed at 900C. From the spectra it is clear that band edge for the as deposited ZnO films is 383 nm with only slight

variation with increase in annealing temperature. Moreover, the interference fringes indicate that all the ZnO films had optically smooth surfaces and no any optical inhomogenities excepts for the film annealed at 900C. There are no good interference fringes and transmittance is also below 80% throught the wavelength range. This can be attributed to the mainly two things first inhomogenity due to tetragonal Zn_2SiO_4 phase present in the film and substrate interface and the platelets kind of structure observed at the surface of film which is evident from the cross sectional SEM image.

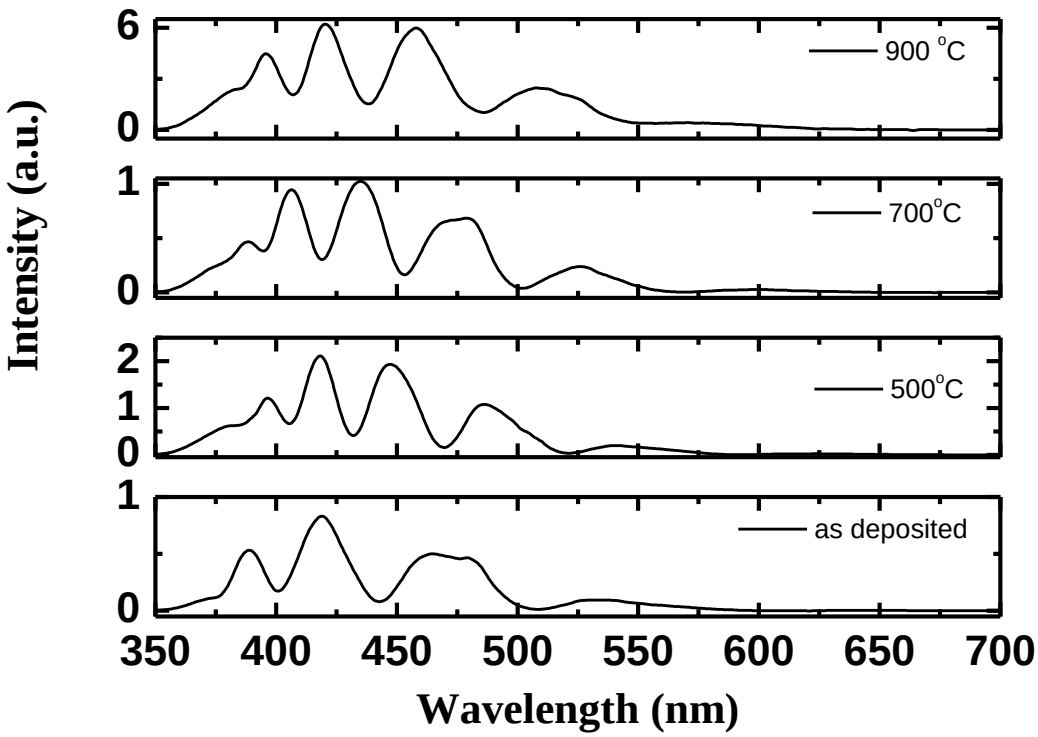


Figure 6: PL spectra for the ZnO films grown on Si substrate with different annealing temperature.

Fig. 6 shows the PL spectra of the ZnO films taken at RT for the as deposited and annealed films at 500C, 700C & 900C. In the spectra of as deposited ZnO film four peaks has been seen. The first peak located at 389 nm which is attributed to the recombination of the free excitons. The second peak at 419 nm in the violet region may be due to radiative defects related to the interface traps existing at the grain boundaries and emitted from the radiative transition between this level and the valence band [13]. The third broad peak observed in the blue region can be devoted to the oxygen vacancies in the film. Oxygen vacancies can produce two defects donor level and shallow donor level which lies below the conduction band [14]. The fourth peak observed is weak and located in the green region around 540 nm is due to recombination via surface localized states owing to the ionized oxygen vacancies (V^+_o) [15].

After annealing the peak at 389 nm attributed to recombination of free exciton becomes weak for the films annealed at 700C while disappear for the other higher annealed films. At 395 nm in the violet region the peaks are observed in case of 500C & 900C annealed films. This can be attributed to the photogenerated electron transit from conduction band to valance band [16]. For the 700C annealed film the peak located at 406 nm can be attributed to the transition from bottom of the conduction band to the V_{Zn} level [17]. The peak observed at 419 nm in as deposited films disappears for the films annealed at 700C but in other two annealed films it remains as it is. Now, in the blue region two sharp peaks are observed. The origin of these peaks is still not understood yet. In the green region, at 540 nm peak is observed for the 500C annealed films while for other two films annealed at higher temperature the peak observed at around 520 nm which is well matched with the energy interval between the bottom of the conduction band and O_i level [18].

6. CONCLUSION:

The high quality ZnO films have been deposited on Si and amorphous silica substrate using RF magnetron Sputtering at ultrahigh vacuum in an only Ar atmosphere. The post annealing has been done at different temperatures in air. All the ZnO films grown have been showed a Hexagonal wurtzite structure and preferably oriented in (002) direction. With increase in annealing temperature crystallinity of the film is improved. In the case of amorphous silica substrate, a small fraction of Zn_2SiO_4 phase detected at 900C while on Si substrate no any other phase is detected. At or above 700 C the films on amorphous silica shows the almost all the reflection from the ZnO plane which is not the case for Si substrate, films remain oriented up to 900C annealing temperature this deterioration of orientation of film may results due to amorphous nature of silica substrate. Moreover, the observed lattice strain is less for the films grown on Quartz compared to Si. At 900 C the films on Si exhibits larger grain size, and platelets kind of surface which results in drastic decrease in transmittance of the films. The various intrinsic defects of ZnO films are also explained using PL spectra.

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REFERENCES:

1. Rau U. and Schmidt M., (2001): Electronic properties of ZnO/CdS/Cu(In,Ga)Se2 solar cells — aspects of heterojunction formation: Thin Solid Films, 387, 141.
2. Liu Y., Gorla C.R., Liang S., Emanetoglu N., Lu Y., Shen H. and Wraback M., (2000): Ultraviolet detectors based on epitaxial ZnO films grown by MOCVD: J. Electron. Mater., 29, 69-74.
3. Soki T., Hatanaka Y. and Look D.C., (2000): ZnO diode fabricated by excimer-laser doping: Appl. Phys. Lett., 76, 3257.
4. Zobinski J. S., Corneille J., Prasad S. V., McDevitt N. T. and Bultman J. B., (1997): Lubricious zinc oxide films: synthesis, characterization and tribological behaviour: J. Mater. Sci., 32, 5313-5319.
5. Hickemell F. S., (1985): From PGUE to G-SU to UFFC-S, 1953-1997 a historical perspective : IEEE Trans. Sonics Ultrason. SU, 32, 62.
6. Jenkins D. F. L., Cunningham M. J., Velu G. and Remiers D., (1997): The use of sputtered ZnO piezoelectric thin films as broad-band microactuators: Sens. Actuators A, 63, 135-139.
7. Kamalasanan M.N. and Chandra S., (1996): Sol-gel synthesis of ZnO thin films: Thin Solid Films, 288, 112-115.
8. Im S., Jin B.J. and Yi S., (2000): Ultraviolet emission and microstructural evolution in pulsed-laser-deposited ZnO films: J. Appl. Phys., 87, 4558.
9. Li B.S., Liu Y.C., Shen D.Z., Zhang J.Y., Lu Y.M. and Fan X.Q., (2003): Effects of RF power on properties of ZnO thin films grown on Si (0 0 1) substrate by plasma enhanced chemical vapor deposition: J. Cryst. Growth, 249, 179-185.
10. Zhang Y., Du G., Liu Dali, Wang J., Wang X., Ma Y., Wang J., Yi J., Yang X., Hou X. And Yang S., (2002): Crystal growth of undoped ZnO films on Si substrates under different sputtering conditions: J. Cryst. Growth, 243, 439-443.
11. Ko H.J., Chen Y.F., Zhu Z., Yao T., Kobayashi I. and Uchiki H., (2000): Photoluminescence properties of ZnO epilayers grown on CaF2(111)CaF2(111) by plasma assisted molecular beam epitaxy: Appl. Phys. Lett., 76, 1905.
12. Yamada A., Sang B. and Konagai M., (1997): Atomic layer deposition of ZnO transparent conducting oxides: Appl. Surf. Sci., 112, 216-222.
13. Jin B.J., Im S. and Lee S.Y., (2000): Violet and UV luminescence emitted from ZnO thin films grown on sapphire by pulsed laser deposition: Thin Solid Films, 366, 107-110.
14. Wang Q.P., Zhang D.H., Ma H.L., Zhang X.H. and Zhang X.J., (2003): Photoluminescence of ZnO films prepared by r.f. sputtering on different substrates: Appl. Surf. Sci., 220, 12-18.
15. Sharma Prashant K., Pandey Avinash C., Zolnierkiewicz Grzegorz, Uskos Nikos G and Rudowicz Czeslaw, (2009): Relationship between oxygen defects and the photoluminescence property of ZnO nanoparticles: A spectroscopic view: J. Appl. Phys., 106, 094314.
16. Wei Huiying, Wu Youshi, Wu Lili and Hu Chunxia, (2005): Preparation and photoluminescence of surface N-doped ZnO nanocrystal: Mater. Lett., 59, 271-275.
17. Teng X.M., Fan H.T., Pan S.S., Ye C. and Li G.H., (2006): Photoluminescence of ZnO thin films on Si substrate with and without ITO buffer layer: J. Phys. D: Appl. Phys., 39, 471.
18. Lin Bixia, Fu Zhuxi and Jia Yunbo, (2001): Green luminescent center in undoped zinc oxide films deposited on silicon substrates: Appl. Phys. Lett., 79, 943.