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LETTER TO THE EDITOR

Formation mechanism of Zn_2SiO_4 crystal and amorphous SiO_2 in ZnO/Si system

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Abstract

In our recent study Xu *et al* (2002 *Chem. Phys. Lett.* **364** 57–63), a phase transformation from the hexagonal to the tetragonal structure in the annealed ZnO films on silicon was studied by atomic force microscopy. Cathodoluminescence (CL) and glancing-angle x-ray diffraction analysis of the ZnO films indicated that such a transformation is due to the generation of a tetragonal zinc silicate. In order to identify the formation mechanism of the zinc silicate and the bottom broadening of the UV band, a depth profile secondary ion mass spectroscopy experiment was carried out. The results show that vast atomic diffusion between the ZnO film and the silicon substrate occurred due to the annealing temperature. Such interdiffusion can create not only a mixed crystal of ZnO and Zn_2SiO_4 , but also an amorphous silicon dioxide (a- SiO_2) in a deep range from the surface to the interface of the ZnO/Si system. The a- SiO_2 is most probably the source of the 453 nm blue band hidden in the tail of the 390 nm UV band, since the blue band agrees with the CL spectra of the amorphous quartz glass and the thermally oxidized silicon.

ZnO film has been widely studied for a variety of applications in piezoelectric acoustic wave devices [1, 2], varistors [3, 4], optical waveguides [5], substrates or buffer layers for the growth of GaN [6, 7], or as a material for light-emitting diodes [8]. In addition, ZnO deposited on silicate glass has been widely used as a transparent conducting oxide buffer in the construction of semiconductor film solar cells [9]. A ZnO/Si heterojunction was also investigated as a candidate for a mono-junction solar cell [10]. Under such conditions, it is necessary to

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carry out studies of ZnO/Si or ZnO/silicate glasses, which are the important parts of thin-film solar cells.

In our recent study [11], an analysis of atomic force microscopy (AFM), cathodoluminescence (CL) and glancing-angle x-ray diffraction (GXRD) of ZnO films on Si annealed at different temperatures was carried out. The results show that the crystal quality of the film was improved with increasing the annealing temperature, while the hexagonal phase of the ZnO film was transformed into a mixed phase including a hexagonal and a tetragonal phase when annealing at a temperature approaching or higher than 800 °C. On increasing the temperature continuously above 800 °C, such a mixed phase changed into a tetragonal structure. The light emission of the sample also changed from the intrinsic emission of ZnO dominating to the emission of zinc silicate dominating. However, the above analysis did not give a reasonable explanation for the broadening at the low energy side of the bottom tail in the UV band. In order to identify the formation mechanism of the zinc silicate and to find the reason for such broadening, a depth profile secondary ion mass spectroscopy (DSIMS) analysis was used in this work. Combining DSIMS, GXRD and further CL analysis of the amorphous quartz glass and the thermally oxidized silicon, an amorphous silicon dioxide (a-SiO₂) was found to be created in the ZnO film.

The samples in this work are the same as those used in the previous work [11]. A reactive DC sputtering method was chosen to grow the ZnO film on silicon. The target was a zinc disc with 4N purity. Before inserting it into the vacuum chamber, the Si(100) substrate was treated by a 5% HF solution for 3 min to remove silicon oxide on the Si surface. The growth procedure progressed in two steps: first, sputtering a Zn buffer layer with a thickness of about 50 Å at room temperature in pure Ar gas; then sputtering a ZnO film with thickness of about 2000 Å at 400 °C in a gas mixture of 50% Ar + 50% O₂. The pressure of the chamber during deposition was 2×10^{-2} Torr. The sputtering power was 15 W. After sputtering, four samples were separated from the main one. Sample 1 is the as-grown sample, the other three were annealed in ambient air for 1 h at different temperatures 600 °C (sample 2), 800 °C (sample 3) and 950 °C (sample 4). In order to obtain a detailed picture of the atomic diffusion present in the ZnO/Si system, we investigated a depth profile of four elements (P, Si, O and Zn) in samples 1 (as-grown) and 3 (800 °C, 1 h annealing) using DSIMS, as shown in figure 1. The reason the element P was chosen is that the silicon substrate is P-doped. Discussions from figure 1 are as follows:

- (i) *Distribution of P element*: although sample 1 is as-grown, the growth temperature was as high as 400 °C, which was enough to cause a segregation effect of P diffusing from the substrate to the ZnO surface and forming a P peak near the surface. DSIMS counts for the P peak are 1.4×10^2 . For sample 3 annealed at 800 °C, P was more concentrated near the surface region with the peak value 2×10^2 . Since the DSIMS yields in figure 1 are in exponential units, such a segregation effect could be seen to be very strong. However, since the P content in the ZnO/Si system is very small due to the carrier concentration in the silicon substrate being only $1.2 \times 10^{16} \text{ cm}^{-3}$, the influence of P and its compounds on the luminescence is fairly weak. On the other hand, the influence of P on the electric transport in the ZnO/Si heterojunction should not be neglected, which needs further study.
- (ii) *Distribution of Si and the formation of SiO₂*: as was shown in figure 1, the Si curve in the substrate is lower than that in the film. This is because the DSIMS yields in the film are greater than those in the substrate. Si exists as a monoelement in the substrate but as a compound in the film. Compared to sample 3, although the diffusion of Si to the film surface was found in sample 1, the silicon component in the near-surface region (0–0.07 μm) is 2.5 times lower than that in the far-to-surface region (0.08–1.5 μm). This

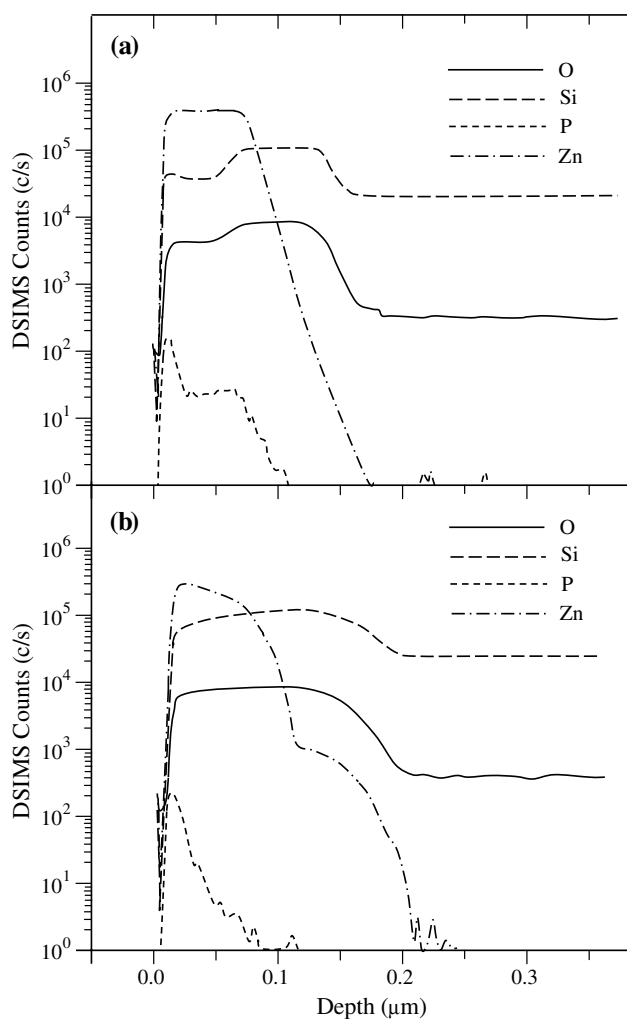


Figure 1. Depth profile secondary ion mass spectroscopy (DSIMS) of (a) sample 1 and (b) sample 3.

fact indicates that a great deal of silicon compound was not formed in the near-surface region, but formed in the far-to-surface region because the Si curve is almost parallel to the O curve in this region. However, this condition was significantly changed in sample 3. The silicon component in the near-surface region is 2.5 times than that found in sample 1 and the Si curve is almost parallel to the O curve in the whole film region, which indicates that oxidized silicon was probably formed in the ZnO film after annealing in the air at 800 °C for 1 h.

- (iii) *Diffusion of Zn and O and the formation of zinc silicate:* a vast diffusion of Zn was found in sample 1, although the annealing temperature is only 400 °C. The Zn curve is parallel to the O curve only in the near-surface region. This fact indicates that a good stoichiometry of Zn and O only existed in the near-surface region. A silicon-based compound is formed in the far-to-surface region, in which vast diffusion of Zn results in more and more oxygen combining with the silicon and leads to the increase of the Si and O curves. Compared to sample 1, about 70% of Zn diffused to the far-to-surface region in the film of sample 3.

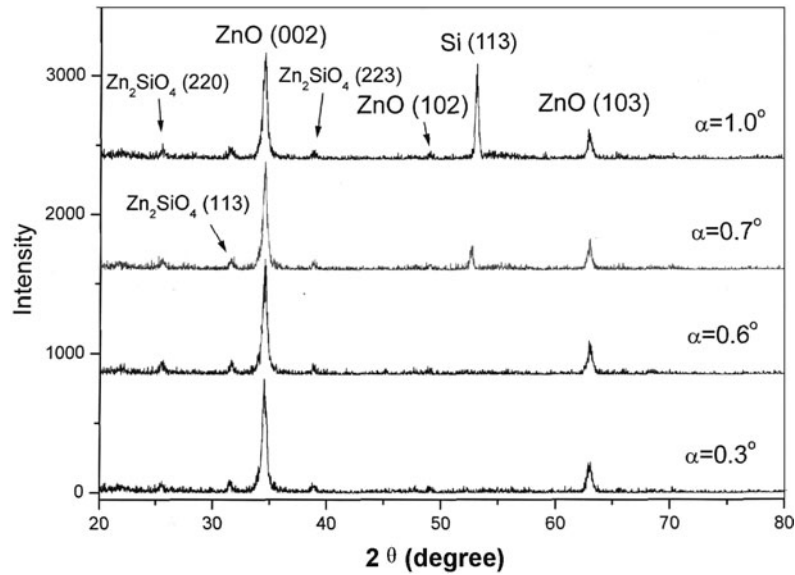


Figure 2. GXR D spectra from sample 3 with different incident angles of 0.3° , 0.6° , 0.7° and 1.0° (from the bottom to the top), respectively.

The loss of Zn is very obvious except in a very thin surface layer ($0\text{--}0.03\ \mu\text{m}$). Note that the O curve does not exactly parallel the Si curve in the near-surface region but is increased by two times (compared to a dummy curve parallel to the Si curve). The fact indicates the formation of a silicate compound in the near-surface region. In the ZnO/Si system, the compound is most probably Zn_2SiO_4 .

Based on the above DSIMS analysis, two probable silicon compounds were found in the ZnO films on silicon. In our previous work [11], the formation of crystal Zn_2SiO_4 in the ZnO film was shown by GXR D. The principle of GXR D and the GXR D curves of samples 1 and 4 measured at the incident angle $\alpha = 1.0^\circ$ were also shown in [11], in which the tetragonal Zn_2SiO_4 structures were found in sample 4. Figure 2 is the GXR D spectra of sample 3 measured at different α . The 2θ scanning curves corresponding to the conditions of choosing $\alpha = 0.3^\circ$, 0.6° , 0.7° and 1.0° are shown in the figure from the bottom to the top. The ZnO (002), (102), (103) and (220) peaks occurred in every curve. This is different to the result of ' $\theta\text{--}2\theta$ ' XRD, in which only a ZnO(002) peak could be clearly found. The Si(113) peak occurred while α is equal to or greater than 0.7° and drifts to a larger degree when α is increased. Therefore, the x-rays have already passed through the film and touched the silicon substrate while $\alpha = 0.7^\circ$. It is interesting to find that the Zn_2SiO_4 (200), (113) and (223) peaks also appeared in all the curves, which indicate the formation of the compound in the whole ZnO film. Although the relation between the peak intensity and the component is not exactly linear, the component of Zn_2SiO_4 is still less than that of ZnO in sample 3, because these Zn_2SiO_4 peaks seem to be much weaker than the ZnO(002) peak.

In the $\alpha\text{--}2\theta$ scanning mode, the film thickness T could be calculated [12] by the following formula:

$$T = \frac{-\ln(1 - I^t/I^\infty) \sin \alpha \sin \beta}{(a\mu_{\text{ZnO}} + b\mu_{\text{Zn}_2\text{SiO}_4} + c\mu_{\text{SiO}_2})(\sin \alpha + \sin \beta)}$$

where I^t and I^∞ are the diffraction intensities of finite and infinite thickness, respectively.

a , b and c are the components of the ZnO, the Zn₂SiO₄ and the SiO₂ in the film, respectively. $\mu_{\text{ZnO}} = 2.38 \times 10^{-5} \text{ nm}^{-1}$, $\mu_{\text{Zn}_2\text{SiO}_4} = 2.68 \times 10^{-5} \text{ nm}^{-1}$ and $\mu_{\text{SiO}_2} = 0.77 \times 10^{-5} \text{ nm}^{-1}$ are the line absorption coefficients of ZnO, Zn₂SiO₄ and SiO₂, respectively. When $\alpha \ll \beta = 2\theta - \alpha$, the formula can be reduced as

$$T = \frac{0.13 \sin \alpha}{a\mu_{\text{ZnO}} + b\mu_{\text{Zn}_2\text{SiO}_4} + c\mu_{\text{SiO}_2}}.$$

The calculated film thicknesses with different a , b and c are: $T = 46.9 \text{ nm}$ (when $a = 1$ and $b = c = 0$), 52.3 nm (when $a = b = 0.5$ and $c = 0$) and 59.2 nm (when $a = c = 0$ and $b = 1$). The results are much smaller than the DSIMS data of sample 3 with the film thickness $0.14 \mu\text{m}$. Therefore, the effect of SiO₂ in the film should not be neglected, although the crystal phase of SiO₂ was not found in the GXR D spectra. Such SiO₂ is most probably amorphous since the crystal SiO₂ is difficult to form below 1100°C . As a matter of fact, the calculated film thickness should be mainly controlled by $c\mu_{\text{SiO}_2}$, because the value of $\mu_{\text{SiO}_2} \ll \mu_{\text{ZnO}}$ or $\mu_{\text{Zn}_2\text{SiO}_4}$. The closest value $T = 140.5 \text{ nm}$ was obtained by choosing $a = 0.1$, $b = 0.05$ and $c = 0.85$. That is, about 85% of the film was transformed into the a-SiO₂ after annealing at 800°C in air for 1 h. This result is in accordance with the DSIMS data (see figure 1(b)).

To search for more evidence of the a-SiO₂ existing in the ZnO film, it is necessary to resolve the CL spectra of the sample. In figure 3(a), three main structures located at 400 nm (UV band), 453 nm (blue band) and 523 nm (green band) were solved with Gaussian symmetry shapes from the CL spectrum of sample 3. Although the UV band, blue band and green band appeared in the CL spectra of all samples, the intensity and the position, as well as the FWHM, of all three bands are different, depending on the annealing temperature. By comparing the CL spectra of pure ZnO and Zn₂SiO₄ in [11], we analysed the reason for the variation of the UV and green bands in which the position of the UV peaks of samples 1, 2 and 3 changed from 380 nm (1) to 387 nm (2) and 400 nm (3), while the intensity of the peaks increased rapidly. This fact indicates that the crystal quality of the ZnO films was improved by increasing the annealing temperature. On the other hand, the redshift of the UV peak is attributed to a renormalization of the forbidden gap and is the result of an 'electron-hole plasma' (EHP) emission mechanism [13]. According to previous studies [14, 15], the green band is formed by transitions from shallow donors to deep acceptors, such a transition being accompanied by a phonon replica process. Also the deep acceptor has a ground state and excited states. In the reported high resolution PL results [12], the modulated peaks occurring in the PL coincide with the difference of the shallow donor level and the deep levels of the acceptor plus an integral multiple of an optical phonon energy. The dominant transition occurs between the shallow donor level and excited states of the deep level. Therefore, the green band is a wide emission band with the peak position at 505 nm . According to the above discussions, a mixed crystal of ZnO and Zn₂SiO₄ was found in 800 and 950°C annealed films. Therefore, the 523 nm green band is the overlap of the 505 nm ZnO green band and the 525 nm Zn₂SiO₄ green band. The 453 nm blue band was also found to appear in all samples annealed at different temperatures. The intensity of the UV and blue bands goes up to their maximum by increasing the annealing temperature up to 800°C , but the intensity decreased on increasing the annealing temperature continuously to 950°C . Therefore, the light emission is mainly from the UV band and the blue band in the ZnO film annealed at 800°C for 1 h. On the other hand, the EHP emission should be Gaussian symmetrical. Therefore, the 453 nm blue band hidden in the tail of the UV band should be attributed to another emission mechanism, even though the blue band was reported as an intrinsic emission belonging to ZnO [16–18].

A new interesting result from the DSIMS measurement shows that the a-SiO₂ may exist in the annealed ZnO film. Although the result was not supported by the GXR D measurement,

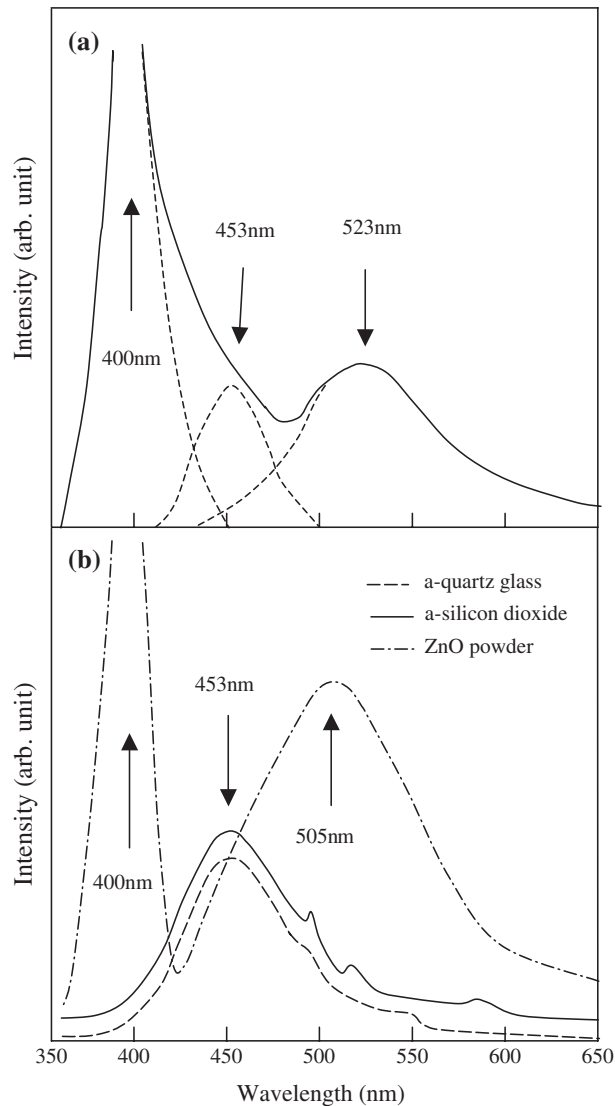


Figure 3. (a) Resolving CL spectrum of sample 3, indicating UV, blue and green bands at 400 nm, 453 nm and 523 nm, respectively. (b) CL spectra of amorphous quartz glass, amorphous silicon dioxide (thermally oxidized silicon) and a pure ZnO powder. To avoid charge accumulation, 1 nm gold film was sputtered onto the surface of the samples.

new evidence of a 453 nm blue band was found by resolving the unsymmetric UV band (see figure 3(a)) of the annealed ZnO film. If the 453 nm blue band originates from the a-SiO₂, then it could be identified from the luminescence spectrum of a kind of SiO₂ compound, such as amorphous quartz glass. The CL spectra of an amorphous quartz glass, a thermally oxidized silicon (fabricated by annealing a silicon wafer in 800–950 °C hot air for an hour) and a ZnO microcrystal powder (with a purity of 4N) are shown in figure 3(b), in which the 453 nm blue luminescence is from an unknown blue centre. Therefore, it should be reasonable if we attribute the 453 nm blue band to the blue centres in the a-SiO₂ in the ZnO film deposited on silicon.

In conclusion, the formation mechanism for the zinc silicate and the amorphous silicon dioxide, in a deep range from the surface to the interface of the ZnO/Si system, can be attributed to atomic thermal diffusion. The analysis of DSIMS, GXRD and CL shows that vast atomic diffusion between the ZnO film and the silicon substrate occurred under high temperature annealing above 400 °C. A result of this report is to correctly identify that such thermal interdiffusion is the only origin of these two silicon compounds. The result suggests improving the popular DC sputtering method to grow ZnO films on a silicon or silicate substrate. In order to decrease the thermal diffusion effect, high temperature annealing must be abandoned. A resolving method is to increase the reaction temperature. Meanwhile, the deposition temperature (substrate temperature) should be significantly decreased.

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