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Improved optical properties of ZnO thin films by concurrently introduced interfacial voids during thermal annealing

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We report the influence of size controlled interfacial voids on the optical properties of non-epitaxial polycrystalline ZnO films grown by atomic layer deposition. Interfacial voids generated due to nanoscale Kirkendall effect [A. D. Smigelskas and E. O. Kirkendall, Trans. AIME 171, 130, (1947)], along the ZnO-Al_2O_3 interface, enhanced the ratio of near band edge to defect luminescence of ZnO films up to eight folds. This improvement is attributed to stress relaxation caused by formation of interfacial voids that allowed greater grain growth within the polycrystalline ZnO films upon annealing. Larger crystals have a lower surface-to-volume ratio profile which lessens the defect emission by decreasing surface effects on the optical properties of ZnO. © *2011 American Institute of Physics*. [doi:10.1063/1.3609321]

Internal and interfacial voids have long been considered as undesirable microstructural defects that impair the mechanical, adhesion, and bonding properties of thin films.[1] These formations also reduce the electrical conductivity and density of the grown layers, sometimes forming pinholes which can possibly negate the purpose of the film as a diffusion barrier or anti-corrosive coating. However, carefully engineered voids have the potential to significantly improve the material properties as opposed to deteriorating them. For instance, Frajtag and his co-workers introduced embedded voids near a sapphire/GaN interface using GaN nanowires during the epitaxial growth of GaN layers to reduce the dislocation density in the film.[2] The introduced voids near the interface acted as traps, terminating dislocations caused by the slight lattice mismatch between the deposited film (GaN) and the underlying substrate (sapphire). This technique was shown to improve the film quality drastically, reducing the dislocation density by two orders of magnitude.

ZnO is a very versatile optoelectronic semiconductor due to its direct band gap of 3.37 eV and large exciton binding energy of about 60 meV at room temperature.[3] Derived from these superior properties, ZnO thin films have found wide applications in sensors, light emitting diodes, laser diodes, and so on.[3] Atomic layer deposition (ALD) is one of the most important innovations to grow high quality ZnO thin films because ALD has proven its efficiency in depositing target films with precise thickness control over a wide range of temperatures.[4] However, similar to most other chemical vapour deposition techniques, there exists a built-in residual stress between the ALD-deposited polycrystalline ZnO films and selected substrates. In order to improve the crystalline quality further, post-annealing of the deposited films at high temperatures is often required. In this article, we report a strategy to enhance the quality of ALD-deposited ZnO films by concurrently introducing Kirkendall voids[5,6] at the film/substrate interface during a thermal annealing process. It is revealed that the intrinsic residual stress in polycrystalline ZnO thin films is more effectively reduced by temperature annealing treatment when interfacial voids of controlled dimensions are produced. The relaxation within the films improves the ratio of near band edge to defect luminescence of the ZnO films up to eight folds by way of reduction of surface effects and increased crystallinity of the films.

The void formation process consists of three simple steps. First, a thin layer of amorphous Al_2O_3 buffer layer is deposited on a Si (100) substrate using trimethylaluminium (TMA) and water as precursors by ALD. Second, an ALD ZnO layer of 40 nm is grown on top of the Al_2O_3 buffer layer, this time using diethylzinc (DEZ) and water as the process gases. Both films are deposited at 150 °C with N_2 as the purge gas. Finally, the deposited films are annealed at 700 °C for three hours in an open furnace to induce the formation of interfacial voids.

Kirkendall voids are formed as a consequence of unequal material transfer between a diffusion couple across an interface.[7] This imbalance in diffusivities causes accumulation and supersaturation of lattice vacancies into voids near the interface, along the side of the faster diffusing species. ZnO and Al_2O_3 are the well studied diffusion couple and represent an extreme case of the Kirkendall effect due to one way diffusion of ZnO into Al_2O_3 accompanied by the formation of spinel $ZnAl_2O_4$.[6,8] Figure 1(a) is a schematic illustration of the interfacial void formation process between the ZnO and Al_2O_3 films. By altering the thickness of the Al_2O_3 buffer layer, the size of the interfacial voids can be easily tuned. On planar surfaces, the void size is directly proportional to the thickness of the Al_2O_3 layer. Hence, Al_2O_3 films of a few nanometers in thickness yield interfacial voids in the same size scale. In order to determine the relationship between the optical properties of the ZnO film and the interfacial voids of different sizes, Al_2O_3 films of 5 nm, 10 nm, and 20 nm were used as a buffer layer.

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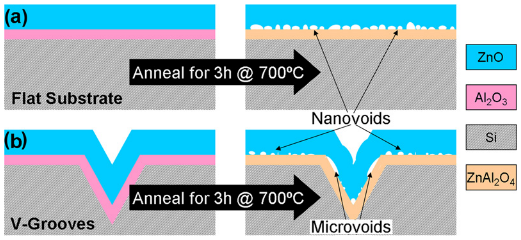

FIG. 1. (Color online) Schematic displaying Kirkendall void formation processes between ALD grown ZnO and Al_2O_3 films on a (a) planar substrate and (b) structured substrate (V-grooves).

Room temperature photoluminescence (PL) was used to study the influence of interfacial voids on the optical and the structural properties of the ALD grown ZnO layers. The measurement setup included a HeCd laser (30 mW, 325 nm) and charge-coupled-device (CCD) camera, as the excitation source and the spectral detector, respectively. Figure 2(a) shows a set of PL spectra obtained from a 40 nm ALD ZnO film before and after annealing without a buffer. As shown in the figure, a typical intrinsic ZnO PL spectrum consists of two characteristic peaks. The first is the near band edge (NBE) peak centered at ~380 nm which is an exitonic transition caused by shallow donors inside the band gap.[9] The second is the defect or deep level emission (DLE) peak with a broad signal that can range from approximately 450 nm to 1000 nm, originating from native defects such as oxygen vacancies, zinc vacancies and zinc interstitials, and etc.[10] In order to implement optical devices operating in the UV region such as light emitting diodes and lasers, a high ratio between the NBE and DLE peaks is desirable. For polycrystalline ALD ZnO films without a buffer layer, a high temperature anneal step improves the NBE/DLE ratio due to the improved crystalline quality, as seen in Figure 2(a). It is observed that this effect is significantly amplified when interfacial voids are created during annealing. The ratio of NBE to DLE is calculated as shown in Figure 2(b). First, the area (A) under the PL curve is calculated from 355 nm to 450 nm using numerical integration. Then, the area (B) under 450 nm to 1000 nm is numerically integrated. Subsequently, the ratio (R) of NBE to DLE is calculated by dividing (A) by (B). We chose integrals over single peak values because small variations may occur from sample to sample which may slightly shift the peak positions. We finally calculated the improvement factor by dividing the (R) values after annealing by the (R) values of the as-grown samples ($R_{annealed}/R_{as\text{-}grown}$). The results are shown in Figure 2(c). It is confirmed that with increasing interfacial void size (increasing Al_2O_3 buffer thickness), a significant increase in the NBE to DLE ratio is observed. In nanostructured ZnO, it is well known that surface effects play a major role in controlling the material properties due to high surface-to-volume ratio.[11,12] Segregated impurities, defects, and adsorbed gasses on the ZnO surface can act as sources and sinks of electrons and influence the associated space charge region.[13] Therefore, decreasing the surface-to-volume ratio by increasing the crystallite size in polycrystalline ZnO thin films improves the NBE to DLE ratio.[14] Voids in thin films can nucleate in response to a locally applied mechanical stress that serves as a relaxation mechanism.[15] Previous reports have shown that high temperature treatment increases the average grain size in thin films and this can increase the applied stress among grains and the underlying surface.[16] When the engineered Kirkendall voids are introduced into the film, they can aid in improving crystallinity in two ways. First, the voids would reduce the locally induced thermo-mechanical stress due to increasing grain size during annealing, and this relaxation would allow further grain growth in the film. Second, the voids can act as free surfaces and enhance mass transport via surface diffusion, facilitating even greater grain growth.[17] Analysis of our samples by SEM confirmed that the buffer layer thickness has a direct association with the grain size (i.e., the thicker the buffer layer, the larger the grains).

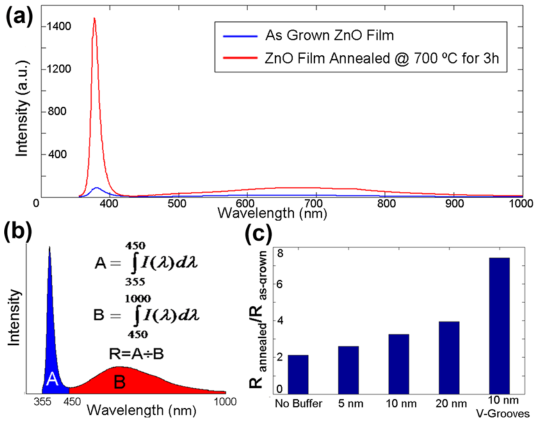

FIG. 2. (Color online) (a) Photoluminescence spectra of a 40 nm ALD ZnO film before and after annealing for three hours without a buffer layer, (b) method used for calculating the NBE/DLE ratio, and (c) graph correlating the NBE/DLE ratio before and after annealing with the corresponding Al_2O_3 buffer layer thicknesses (i.e., interfacial void size).

Additionally, interfacial voids can be enlarged to a few micrometers by changing the surface geometry of the base substrate. The interfacial void development on a structured substrate, in this case a 20 μm wide and 14 μm deep V-groove into Si (100), can be seen in Figure 1(b). The influence of geometrical changes on the Kirkendall void formation in the presence of a stress gradient have already been investigated.[18] During thermal annealing, Kirkendall voids preferentially form in the relatively high stress regions on a structured substrate due to increased vacancy flow into these areas. These voids can reduce the adhesion between the film and the substrate, initiating blistering due to thermal mismatch. Please note that, we have repeated the same experiment without the Al_2O_3 buffer layer (only 40 nm ZnO film) and did not observe any large voids after the anneal, suggesting blistering is indeed initiated by the Kirkendall voids. These structures represent the collective macro effect of the nanoscale Kirkendall effect. Figure 3 shows a series of images comparing the surfaces from a planar sample (Figure 3(a)) with 10 nm Al_2O_3 buffer layer and a structured sample (Figures 3(b)–3(d)) with a buffer layer of the same thickness, after annealing. As expected, the planar sample exhibits no large voids when observed from the top, even when observed up-close. This is because of the small size of the interfacial Kirkendall voids embedded between the ZnO and $ZnAl_2O_4$ layers after the solid state reaction. On the other hand, very large voids are present inside the V-grooves on the structured sample when

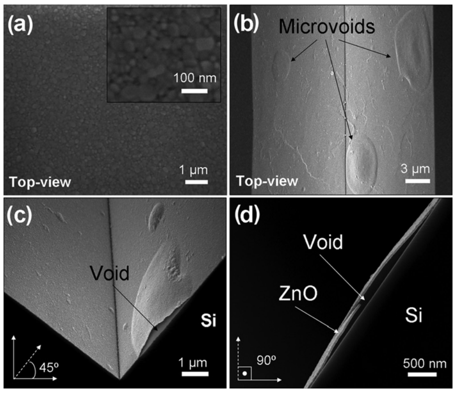

FIG. 3. SEM image of (a) the surface of a planar sample with 10 nm Al_2O_3 buffer layer after annealing: inset showing a magnified version (b) the surface of a structured (V-groove) sample with the same Al_2O_3 buffer layer thickness after annealing (c) 45°-tilted view of the V-groove and (d) 90°-tilted cross-sectional view of the same V-groove.

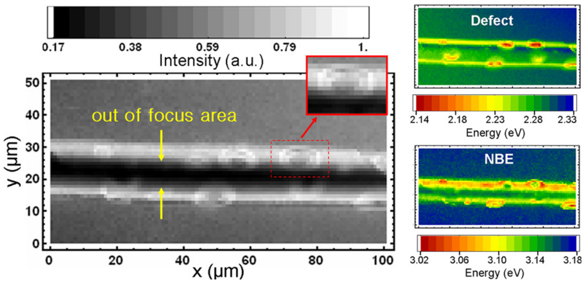

FIG. 4. (Color online) (Left) Micro-PL mapping of the defect spectrum from a structured substrate (V-groove) with a 10 nm Al_2O_3 buffer layer after annealing and (Right) first momentum maps of defect and near band edge spectra.

observed from the top as displayed in Figure 3(b). In addition, the 45°-tilted (Figure 3(c)) and cross-sectional (Figure 3(d)) micrographs reveal that the large interfacial voids create locally freestanding ZnO layers, physically separating the active layer from the buffer layer. As can be seen in Figure 2(c), these large voids further improved the NBE/DLE ratio up to eight folds which is significantly higher as compared to the planar sample with the same Al_2O_3 thickness. This result correlates well with the above findings that interfacial voids improve NBE/DLE ratio.

In order to study the precise local effects of interfacial voids and confirm the results presented above, high spatial resolution micro-PL mapping was conducted for this sample (etched V-grooves, 10 nm Al_2O_3 buffer). Figure 4 shows the obtained micro-PL maps. At each scanning point, a spectrum of the sample was taken. The integrated intensity between 450 and 660 nm from these spectra provides the calculated defect emission as shown in Figure 4 (left). Due to sample geometry and optical limitations (i.e., depth of focus), the centre of the groove was shifted out of focus. This area is marked in the figure. As shown in the acquired PL map, several microvoids are clearly visible and the defect emission in and around them varies significantly. The portion of the ZnO film sitting on the voids appears to have a much lower defect emission (darker contrast) compared to the areas surrounding the voids (lighter contrast). The inset shows a magnified view of one of the mapped voids. Reduced defect emission on top of the voids confirms our previous findings that interfacial voids improve crystallinity and optical properties. We also calculated the first momentum maps for the NBE and the defect (i.e., DLE) spectra as shown in Figure 4 (right). The first momentum (M_1) of a given spectrum is a quick and accurate way of determining its main emission energy and is given by $M_1 = \frac{\int_b^a Counts(h\nu)h\nu d\nu}{\int_b^a Counts(h\nu)d\nu}$, with a and b the limits of integration, ν the frequency, h the Planck constant, and $Counts(h\nu)$ is the spectrally resolved count rate of the spectrometer. Interestingly, the first momentum NBE map shows that there is a blue shift in the peak value of the NBE emission above the large voids. This result indicates that the decreased surface influence may reduce the dominance of certain types of shallow donors in the ZnO crystallites. In the case of defect emission, a red shift is clearly visible which reveals that larger and better quality ZnO crystals also have fewer higher energy deep level defects as a result of decreased surface-to-volume ratio.

In summary, we have presented an approach for improving optical and structural qualities of non-epitaxial ZnO polycrystalline thin films using interfacial voids generated by the nanoscale Kirkendall effect. Interfacial voids improved the NBE/DLE ratio by as much as eight folds via relaxing the local stresses generated among ZnO grains and creating free surfaces that accommodated enhanced mass transport and grain growth. This, in turn, decreased the surface-to-volume ratio of the ZnO crystals in the film reducing the influence of defects residing on the crystallite surfaces. This proof-of-concept approach is expected to be extended to other material systems.

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