

RESEARCH ARTICLE

Cathodoluminescence study of defects in thermal treatment of zinc titanate thin films deposited by a cosputtering process

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The effects of thermal treatment of polycrystalline ZnO–TiO₂ systems on their luminescence emission and phase properties were investigated using ex situ cathodoluminescence and backscattering electron microscopy. The main features of the spectrum are a blue band at 2.75 eV for the phase of TiO and a complex visible band at 2.18 eV for the phase of ZnO, whose peak intensity depends on the annealing temperature. The spectrum intensity is dominated by the ZnO phase when annealing temperature was 720°C, which is attributed to abnormal grain growth. Competition is observed between the broad band peaked at 2.18 eV and visible band peaked at 2.75 eV as the annealing temperature changed (820°C–920°C). The cathodoluminescence density is gradually governed by the TiO₂ phase, and the emission in polychromatic and monochromatic imaging is stronger equally at 920°C. The nucleation of the TiO₂ and ZnO grains is present in the backscattering electron images as well.

KEYWORDS

backscattering electron microscopy, cathodoluminescence, radio frequency magnetron cosputtering

1 | INTRODUCTION

The ZnO–TiO₂ system has attracted considerable attention because of its many applications as an inorganic compound. Three compounds exist in the ZnO–TiO₂ system¹: Zn₂TiO₄ (cubic), ZnTiO₃ (hexagonal), and Zn₂Ti₃O₈ (cubic). The electrical and chemical properties of the compounds in the ZnO–TiO₂ system make them attractive for a range of commercial applications, for example, white pigment, catalytic sorbent,^{2–4} microwave dielectric materials,⁵ gas sensors,⁶ high performance catalysts,^{7,8} and luminescent materials. ZnTiO₃ can be prepared by solid-state reaction, sol-gel,⁹ bulk manufacture,¹⁰ and chemical vapor deposition.¹¹ In recent years, Radio frequency (RF) sputtering has been applied to produce the stable state of pure ZnTiO₃ (hexagonal phase), which can exist after annealing between 700°C and 800°C. The crystalline phases ZnTiO₃ (hexagonal) and TiO₂ (rutile) could be coexisted at the annealing temperature of 600°C.¹² However, the decomposition from hexagonal ZnTiO₃ to cubic Zn₂TiO₄ and rutile TiO₂ occurs at 920°C.¹³ Meanwhile, single-phase Zn₂Ti₃O₈ films were prepared at temperatures lower than the sintering temperature of the bulk specimen.¹⁴ Earlier, we have concluded that the mechanical properties of the ZnO–TiO₂ system can be changed through its

microstructures, grain sizes, and morphologies.^{15,16} The real risks of this meta-stability in the ZnO–TiO₂ system to its applications has not yet been discussed in the literature. Markedly, the ZnO–TiO₂ system has attracted much attention for its optical properties. For example, ZnO–TiO₂ core-shell nanorods have improved UV photoresponse sensitivity.¹⁷ Lin et al have found that based on the composite of ZnO nanorods and TiO₂, the band edge emission of ZnO nanorods can be enhanced up to 120 times.¹⁸ For optoelectronic devices, doped ZnO films have also been deposited.^{10,19–22} The properties of the ZnO–TiO₂ system that are responsible for the luminescence performance therefore becomes an interesting issue. Therefore, it is believed that the emission mechanism of ZnO–TiO₂ system needs to be evaluated using the cathodoluminescence (CL) technique. The CL spectra for ZnTiO₃ (hexagonal), Zn₂Ti₃O₈ (spinel), and Zn₂TiO₄ (cubic) prepared with different annealing temperature are acquired, and the emissions were studied in detail using CL mapping.

In this report, the author analyzed Zn–Ti–O films, where ZnTiO₃ was the phase, using the CL spectrum and CL mapping to improve the understanding of thermal treatment on the emission. In addition, backscattering electron (BSE) imaging was also used to observe the dominant Zn and Ti phases. Subsequently, the performance of the

resulting ZnTiO₃ films were examined as a function of the phases present and annealed.

2 | EXPERIMENTAL DETAILS

The ZnTiO₃ films were prepared using an RF magnetron cosputtering system using a 4-in-diameter sintered ceramic target (Zn and Ti). To deposit stoichiometric ZnTiO₃ films on the Si substrate, an Ar–O₂ flow (8:2) with a purity of 99.999% at a flow rate of 50 sccm was introduced into the chamber using mass flow controllers, and an RF power of 200 W was used. In addition, the sputtering pressure was 2×10^{-2} Torr; the substrate temperature was set at 250°C; and the duration of the deposition was 1 hour. To remove the contaminants formed on the target surface and to stabilize the sputtering conditions, it was necessary for presputtering to be performed for 5 minutes prior to each deposition process. The specimens produced were subsequently subjected to ex situ thermal treatment at 720°C, 820°C, and 920°C in a furnace under N₂ gas for 2 hours using a heating rate of 5°C/min. The films were ca 220 nm in thickness. The detailed deposition conditions of the ZnTiO₃ films have been provided in previous articles.^{15,16}

After deposition, the surface roughness and microstructure were analyzed using AFM (Veeco Dimension 5000, Scanning Probe Microscopy, D5000). Scanning electron microscopy (SEM) and BSE imaging (JEOL JSM-7001F, operated at 10 keV and 10 nA) were used to observe the surface morphology and elemental distribution, respectively. The effects of thermal-induced phase transformation on the luminescence properties of the ZnTiO₃ films were characterized at 300 K through CL spectroscopy and SEM (JEOL JSM-7001F, operated at 30 keV and 18 nA). The spot size of the electron beam was less than

TABLE 1 The RMS values of ZnTiO₃ with respect to the annealing temperatures

ZnTiO ₃	RMS, nm
RT	3.1
720°C	6.2
820°C	19.5
920°C	21.6

10 nm under these conditions. The CL emissions were collected as polychromatic mapping and monochromatic mapping images.²³ The CL signals were measured using a Horiba Jobin-Yvon iHR550 0.5-m monochromator and detected by a liquid N₂-cooled charge coupled device with an energy resolution of 0.3 meV.

3 | RESULTS AND DISCUSSION

Figure 1 shows the AFM images (5 × 5 μm) of the ZnTiO₃ films deposited on a silicon substrate. The surface roughness (RMS) increased with increasing annealing temperature, with roughness values of 3.1, 6.2, 19.5, and 21.6 nm for annealing temperatures of RT, 720°C, 820°C, and 920°C, respectively (Table 1). From our previous report,¹⁵ a similar result was observed where the cavities were due to the evaporation of Zn, and the white particles were TiO₂ after thermal treatment. A trend was noted that the RMS increased with increasing annealing temperature: at 820°C, RMS = 19.5 nm, while at 920°C, RMS = 21.6 nm. Previous reports suggest that increasing the annealing temperature enhanced the atomic mobility and caused the film recovery to result in weak mechanical properties when the films are annealed under elevated temperatures.^{15,16,19}

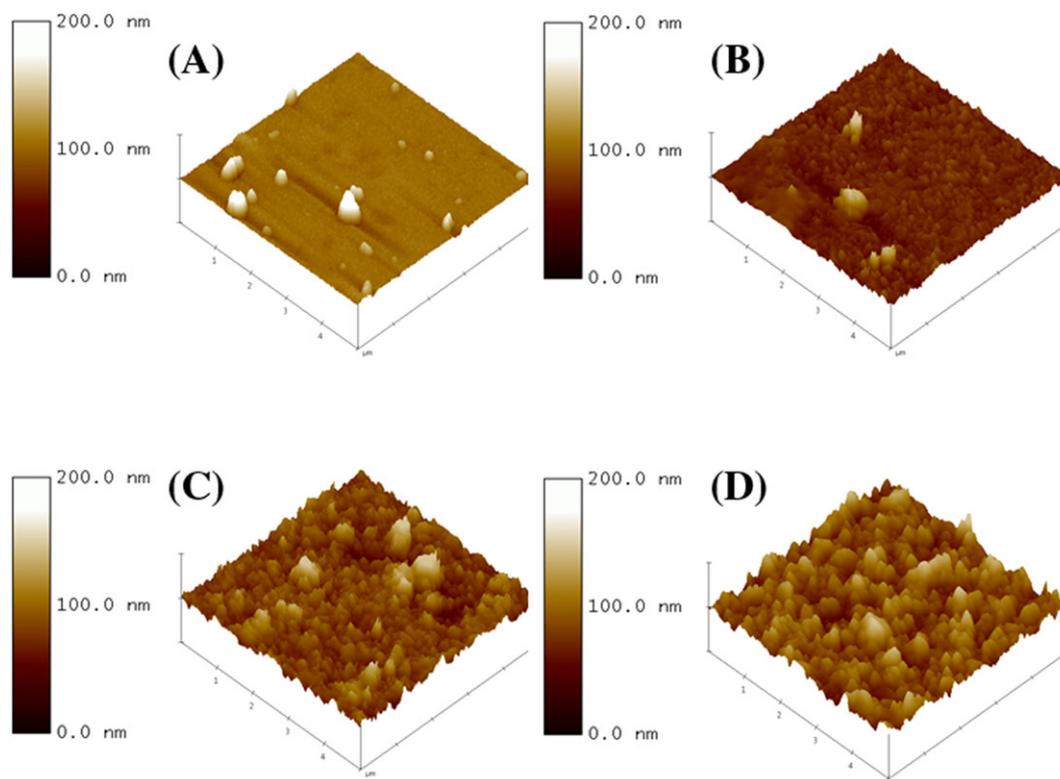


FIGURE 1 3 D-AFM images of the surfaces of ZnTiO₃ films after annealing: A, RT; B, 720°C; C, 820°C; and D, 920°C

Figure 2 shows SEM images of the specimens annealed at 720°C, 820°C, and 920°C. In the SEM and AFM images of those specimens, the particles have larger grain sizes and cover the surface more densely when the annealing temperature increases. The SEM images, CL mapping, and CL spectra are presented in Figure 2. In the specimen prepared without high temperature annealing, labeled RT, the film appears as a plane in the SEM (Figure 2A). The emission is shown in the CL spectrum (Figure 2D) of the RT specimen, which provides a low emission in the visible range and a broad band in the red spectral range centered at 1.9 eV (650 nm). The low emission maybe can be attributed to oxygen vacancy levels or interstitial oxygen defects.^{15,16} Low brightness is obtained in both polychromatic imaging and

monochromatic imaging (Figure 2B,C), which matched the trend of the response of the CL spectrum intensity. Particularly for the monochromatic surface image in Figure 2C, the emission at approximately 2.75 eV (450 nm) is quenched. Therefore, the brightness of the monochromatic image is darker than the polychromatic image (Figure 2B). The polychromatic image reveals that the inner film emits at 2.18 eV (569 nm) and 2.75 eV when annealed at 720°C (Figure 2F). For the specimen annealed at 720°C, the polychromatic image is brighter than the monochromatic image (Figure 2G). The CL spectrum of the annealed (720°C) specimen has a higher visible emission than the RT specimen. The CL spectrum consists of 2 bands that are centered at 2.18 and 2.75 eV (Figure 2H). In the recent work,^{15,16} we found the

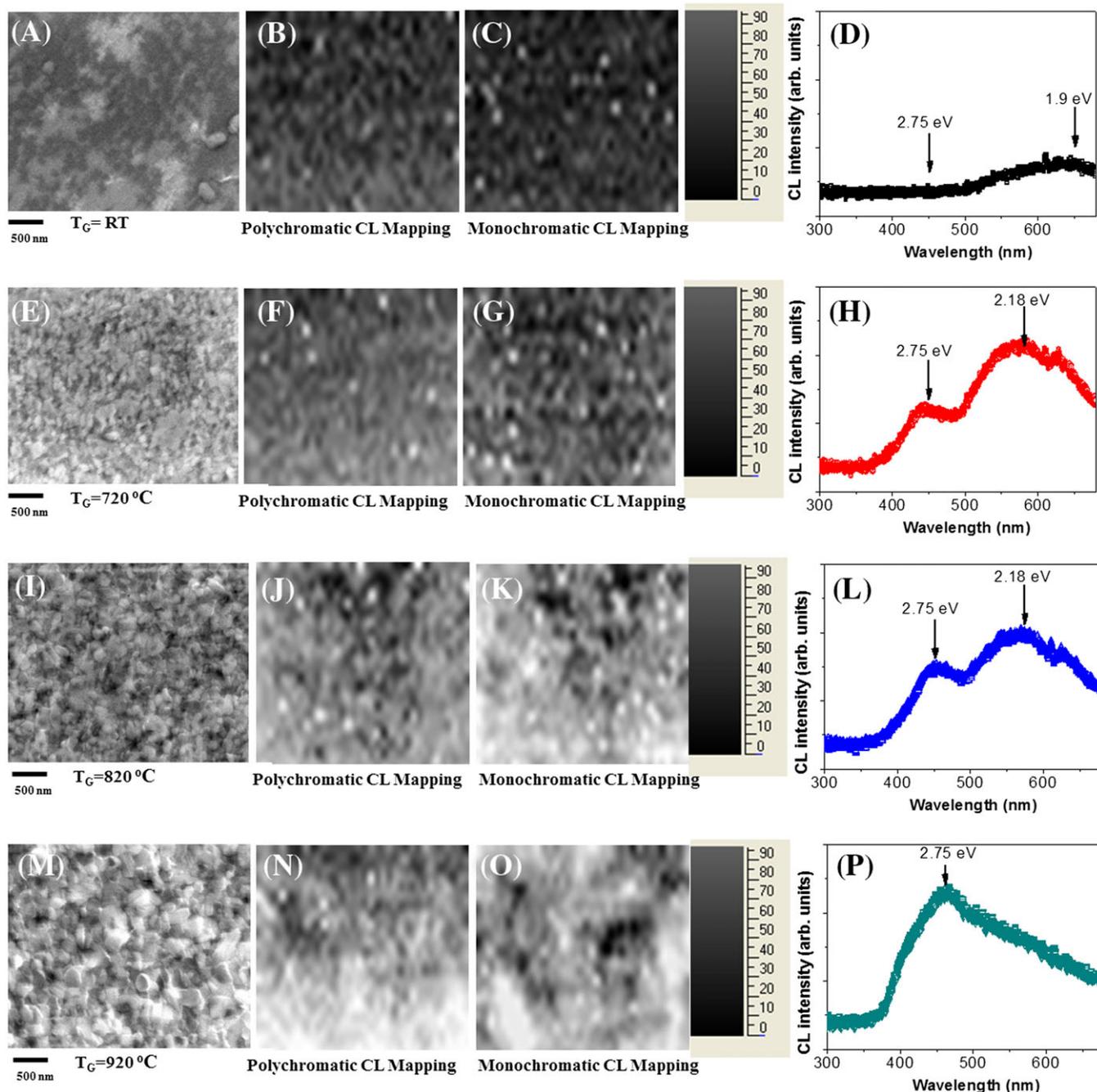


FIGURE 2 Images of ZnTiO₃ samples prepared at different annealing temperatures: RT with A, SEM; B, polychromatic CL mapping; C, monochromatic CL mapping; and D, CL spectrum; 720°C with E, SEM; F, polychromatic CL mapping; G, monochromatic CL mapping; and H, CL spectrum; 820°C with I, SEM; J, polychromatic CL mapping; K, monochromatic CL mapping; and L, CL spectrum; 920°C with M, SEM; N, polychromatic CL mapping; O, monochromatic CL mapping; and P, CL spectrum

increased intensity of the (104) orientation of ZnTiO₃ is obtained in the same samples. The preferred orientation tends to reduce its free energy to reach a stable state as well as to adjust chemical bonding states, which may be the reason for the higher emission efficiency. Many oxygen vacancies are transferred between Zn and Ti; TiO₂ traps electrons; and the shallow traps can act as radiative centers whose emission occurs around 2.75 eV.²⁴ In previous reports,²⁵ annealing sintered TiO₂ in oxygen at 800°C revealed that the centers of crystals are sensitive to oxygen, which agreed with the increased brightness of the monochromatic image of the annealed (720°C) specimen relative to the RT specimen. Otherwise, the brightness of the monochromatic image is still darker than polychromatic image, as shown in Figure 2 F-G. From the intensity of the CL spectrum (Figure 2H), we have observed that the emission intensity of ZnO (2.18 eV) and TiO₂ (2.75 eV) both increased compared to RT. The brightness of the polychromatic image is dominated by the phase of TiO₂ than that of the phase of ZnO when annealed at 720°C. The polychromatic image includes the emission intensity from the ZnO and TiO₂, which produces stronger emission than the monochromatic image (TiO₂ only). Comparing the images of the specimen annealed at 820°C, both the monochromatic and polychromatic images are very close in brightness intensity (Figure 2J,K). However, the intensity for the TiO₂ phase (2.75 eV) in the CL spectrum is increased (Figure 2L), and the intensity of the CL spectrum is higher than that for the film annealed at 720°C (Figure 2H). Hence, the TiO₂ is responsible for the increased emission in the monochromatic imaging when annealed at 820°C. The X-ray diffraction (XRD) patterns of the ZnTiO₃ films show that the (104), (110), (116), and (214) peaks of the hexagonal ZnTiO₃ phase were observed for the annealed (620°C) specimen.¹²⁻¹⁶ For the annealed (820°C) specimen, the intensity of the (104) peak was higher, indicating that the film was highly oriented.¹⁵ The preferred orientation tends to reduce its free energy to reach a stable state as well as to adjust chemical bonding states, which may be the reason for the enhanced emission efficiency at 820°C. The hexagonal ZnTiO₃ decomposes into cubic Zn₂TiO₄ and rutile TiO₂ at higher temperatures but the ZnTiO₃ phase remained stable when annealing temperature was 820°C.²⁶

The RMS values increased (3.1–21.6 nm) with increasing annealing temperature (Table 1). We concluded that the grain size increased when annealing temperature reached 820°C, which causing many vacancies can diffuse more rapidly down boundaries leading to more newly grain boundaries are obtained due to the abnormal grain growth. However, the grain size increased when annealing temperature reached 920°C, which produced the boundaries are regions of high energy they make excellent sites for the nucleation of precipitates and other second- phases, eg, cubic Zn₂TiO₄ and rutile TiO₂ occur from hexagonal ZnTiO₃.¹³ Ageh et al²⁷ have reported that the (104) planes of ZnTiO₃ coatings have extensive stacking faults bordered by partial dislocations, which serve as a pathway for dislocations to glide parallel to the sliding direction for the manner of high temperature solid lubrication. Sun et al²⁸ have discussed that the high stacking fault density (104) is present in ZnTiO₃ textured (104) planes, which provide friction-reducing surfaces/subsurfaces during interfacial sliding. This is the reason why the changes in the luminescence brightness among those samples are sensitive to the annealing temperature. The result of the CL mapping for a hexagonal symmetry is in good agreement

with previous results.^{15,16,27,28} Interestingly, when the same areas are examined, the emission in polychromatic and monochromatic imaging is stronger equally as the annealing temperature was 920°C (Figure 2 N,O). From the CL spectrum (Figure 2P), it is found that the intensity for the ZnO (2.18 eV) is lower than that for the TiO₂ (2.75 eV). The earlier XPS analysis showed that increased chemisorption of oxygen on metal produces a surface layer of adsorbed oxygen when the annealing temperature was 820–920°C.^{15,16} It is suggested that the emission intensity in monochromatic imaging is governed by the quality of the films, which are preferentially related to the TiO₂ phase, for example, cubic Zn₂TiO₄ and rutile TiO₂.¹²⁻¹⁶

ZnO and TiO₂ phases are processed at high temperatures that end up with excessively large grain size (Table 1) and poor mechanical properties.¹⁵ To evidence this problem, BSE analysis is often used to observe the grain growth. The SEM and the corresponding BSE images are presented in Figure 3. The ZnTiO₃ exhibits an increased polycrystalline morphology and a random distribution of particles when the annealing was performed. The BSE images show a dark and rough background with some bright particles scattered over the surface and located at the grain boundaries. Su et al have explored a grain boundary information of Be_{0.4}Zn_{0.6}O films using BSE, and the results are comparable.²⁹ The cavities were not observed by SEM and BSE for the RT specimen because no evaporation of Zn occurred (Figure 3A, B). In a typical decomposition, the small second phases start to appear at the grain boundary (Figure 3C), which is a known step for annealed-induced nucleation. Thus, these bright spots appear to be the TiO₂ dominant phase. Further evidence is provided by the BSE image in Figure 3D. In a BSE configuration, the number of electrons elastically scattered from a phase increases with the increasing atomic number of that phase. Therefore, heavier atoms produce a greater scattering probability. It is noteworthy that some bright spots in the SEM image turn dark in the corresponding BSE images (Figure 3E,F), suggesting that they are composed of elements with a lower atomic number than Zn. The atomic number of Ti (22) is smaller than that of Zn (30); therefore, these darker spots in the BSE image are a Zn-rich phase. The BSE observations matched the trend of the RMS values when the annealing temperature was increased. As the film was annealed at 920°C, the areas consisted of Zn-rich (dark) and Ti-rich grains (light in the BSE image) (Figure 3G,H). This morphology demonstrated a truly mixed Zn and Ti oxide phase, where both types of oxides were distributed randomly since the Zn-rich grains are partially merged with the Ti-rich grains. However, the ZnTiO₃ film has a weak (110) diffraction peak in the XRD pattern when annealed at 820°C. The preferred orientation tends to reduce its free energy to reach a stable state.^{15,16} The trends seen in the earlier XPS and XRD studies provide further evidence that increased oxygen content creates the oxygen-rich regions that are preferentially formed in the TiO₂ phase.¹²⁻¹⁴

In closing, we have analyzed the ZnTiO₃ films, where TiO₂ was using CL technique to improve the understanding of thermal treatment on the emission.³⁰ Noted that, the ZnTiO₃ films have been compared to correlate the localization of the excitonic luminescence and the phase between of the ZnO and TiO₂. The visible band (2.75 eV) could be assigned to excitons bound to grain boundaries in a typical decomposition, which is the reason why strongly CL intensity appear to be the TiO₂ dominant phase.

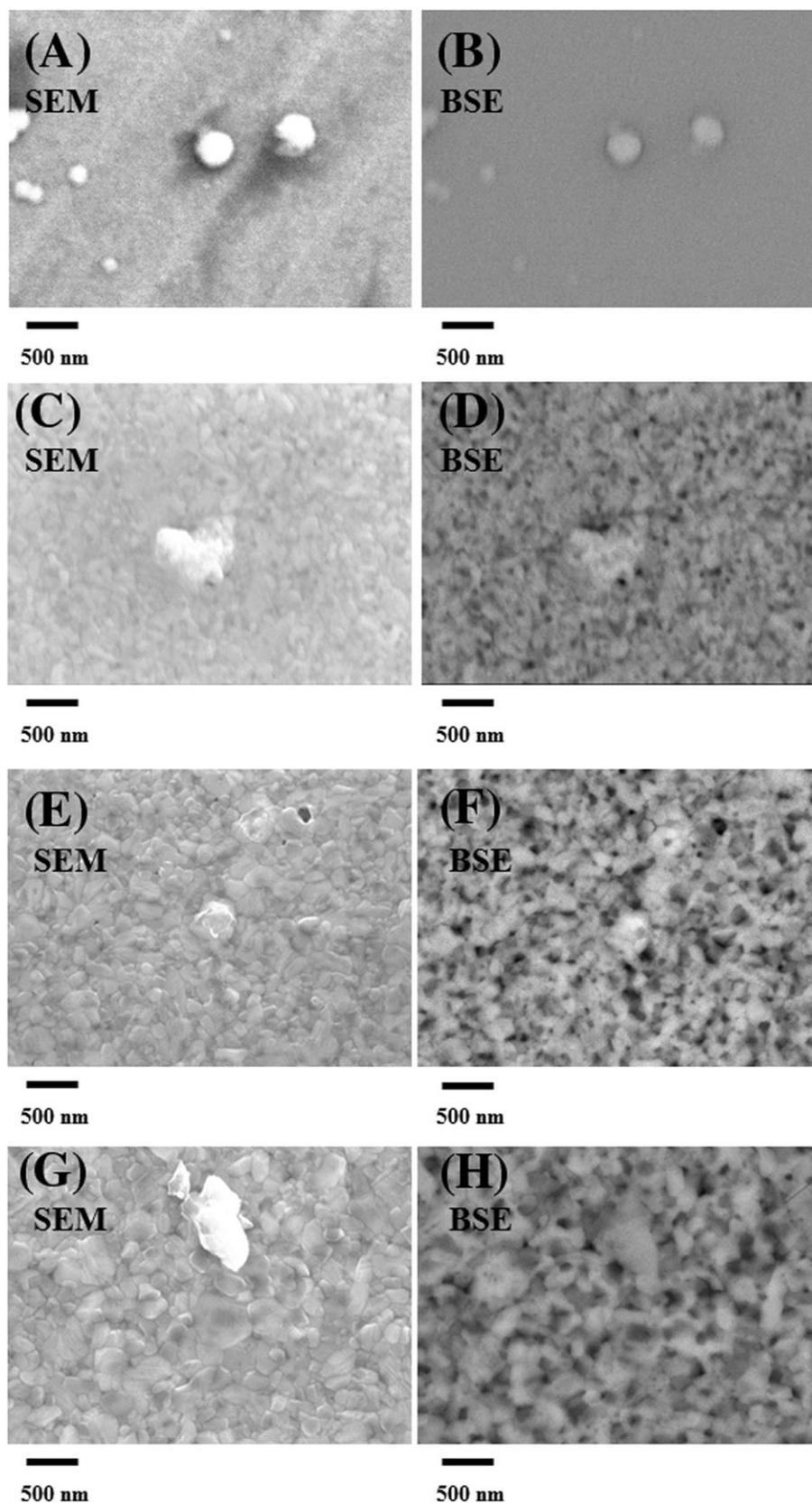


FIGURE 3 SEM and BSE images of ZnTiO_3 thin films treated by conventional annealing conditions: A,B, RT; C,D 720°C; E,F, 820°C; and G,H, 920°C

4 | CONCLUSION

We have characterized RF magnetron cosputtered ZnTiO_3 films using AFM, CL spectrum, and CL mapping. The RMS values measured using

AFM ($5 \times 5 \mu\text{m}$) were 3.1, 6.2, 19.5, and 21.6 nm for annealing temperatures of RT, 720°C, 820°C, and 920°C, respectively. The CL spectra were also used to characterize the luminescence properties of the specimens. An enhanced emission is observed, and the emission

intensity is dominated by the abnormal grain growth and other second-phases, eg, cubic Zn_2TiO_4 and rutile TiO_2 occur from hexagonal ZnTiO_3 at 820–920°C. In addition, the emission might be associated with the increasing grain growth, which is comparable in their effect in polychromatic imaging and monochromatic imaging. Cathodoluminescence spectroscopy has been a very powerful tool for investigating sample quality under a variety of growth conditions. That is why we apply CL to confirm the effective trapping of the threading dislocation and the stacking fault of the samples.

The SEM and BSE observations match the trend of RMS from AFM. A small, regular particle with little grain growth is seen at RT. However, a distribution of grain sizes is produced as the annealing temperature is increased. From the BSE, observations can be seen that the surface was composed of a truly mixed and randomly distributed Zn and Ti oxide areas as well.

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