

Aliovalent Dopant Distribution in Nanocrystalline Tin Dioxide Thin Films Studied by X-Ray Energy Dispersive Spectroscopy

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Tin dioxide (SnO_2) is widely used as gas sensors, catalysts, and transparent electrodes.[1] Tin dioxide thin films are of particular importance due to their excellent electrical properties and possible integration with microelectronic devices.[2] Aliovalent dopants in oxides are electrically and defect compensated in the material. Although much work has been done in empirical electrical property optimization through doping, little is known regarding dopant distribution and segregation at interfaces and defects. In this work we report our studies on the segregation of aliovalent dopants in nanocrystalline SnO_2 films.

Femtosecond pulsed laser ablation of sintered SnO_2 ceramic target was used to fabricate thin films. The targets were nominally doped with different elements to 3 at% using the co-precipitation method. Dopants used were trivalent (Al, In, Yb, Nd, Gd, La) and pentavalent (Nb). Tin dioxide thin films were deposited on Si (001) wafer with a 300 nm thick amorphous SiO_2 layer. Analytical studies were carried out within a field emission gun analytical electron microscope (JEOL 2010F) equipped with an x-ray energy dispersive spectrometer. The probe size used was 1.0 nm, data at grain boundaries were deconvoluted for beam broadening.

Figures 1(a) and 1(b) show plan-view and cross-section TEM images of a SnO_2 thin film. The film has a thickness of 60 nm with a columnar shape and the average grain size of about 20 nm. Figure 2(a) is an HRTEM image showing the microstructure of a SnO_2 film doped with 3 at% Nb. Nb distribution in the film was determined by EDS. An example of Nb concentration profile across a grain boundary in Figure 2(a) is shown in Figure 2(b). For comparison, the line profile of La concentration across a grain boundary in La-doped SnO_2 film is also shown in Figure 2(b). These studies reveal that distinct segregation is observed for the La doped film and no segregation for the Nb-doped film. Figure 3(a) shows the relationship between grain boundary enrichment and dopant size misfit with the host cation. A positive correlation between relative dopant size and grain boundary enrichment can be observed. The fact that pentavalent dopants with similar ionic radius to Sn^{+4} are not severely segregated indicates that the driving force for segregation is elastic strain in the lattice, rather than ionic space charge. In this nanocrystalline films, the number of sites for segregation will be very high which translates in weak segregation profiles compared to theoretical models. The implications of the grain boundary enrichment of dopants on electrical properties are shown in Figure 3 (b). The electrical conductivity in polycrystalline materials is usually dictated by the intergrain barriers. An increase in negatively charged trivalent dopants will decrease the conductivity and the effect will be greater for greater boundary enrichment, as shown in Figure 3(b).

In conclusion, studies of dopant distribution in nanocrystalline tin dioxide thin films show that elastic strain is the driving force for grain boundary segregation at nominal 3 at% doping. Grain boundary enrichment increases the resistivity of the film by increasing the intergrain potential barriers.

[1] V. Demarne and A. Grisel, *Sensors Act B*, **7**, 704 (1992)

[2] G. Sberveglieri, *Sensors Act B* **23**, 103 (1995)

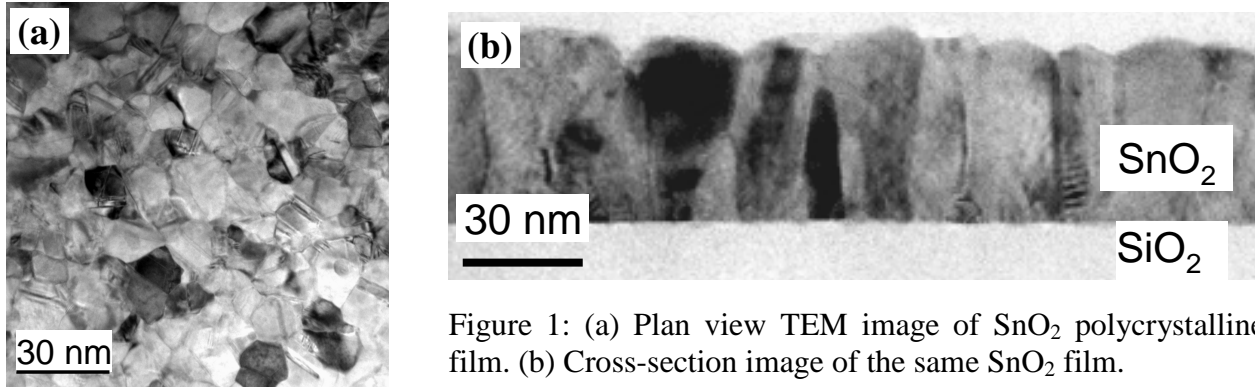


Figure 1: (a) Plan view TEM image of SnO₂ polycrystalline film. (b) Cross-section image of the same SnO₂ film.

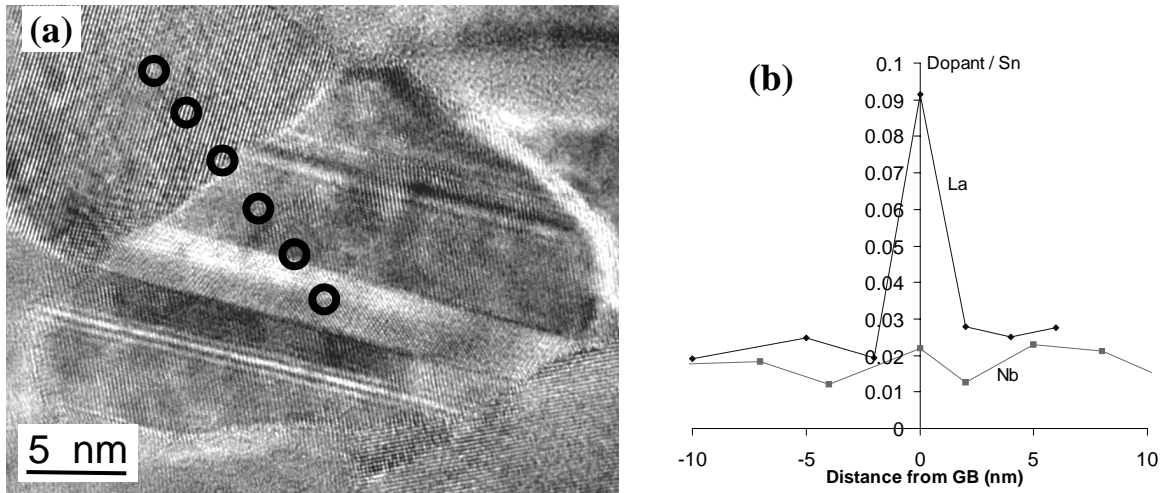


Figure 2 (a) HRTEM image showing the microstructure of Nb-doped SnO₂ film. (b) Nb distribution across the grain boundary in (a), determined by EDS. For comparison, line profile of La concentration across a grain boundary in La-doped SnO₂ film is also shown in (b).

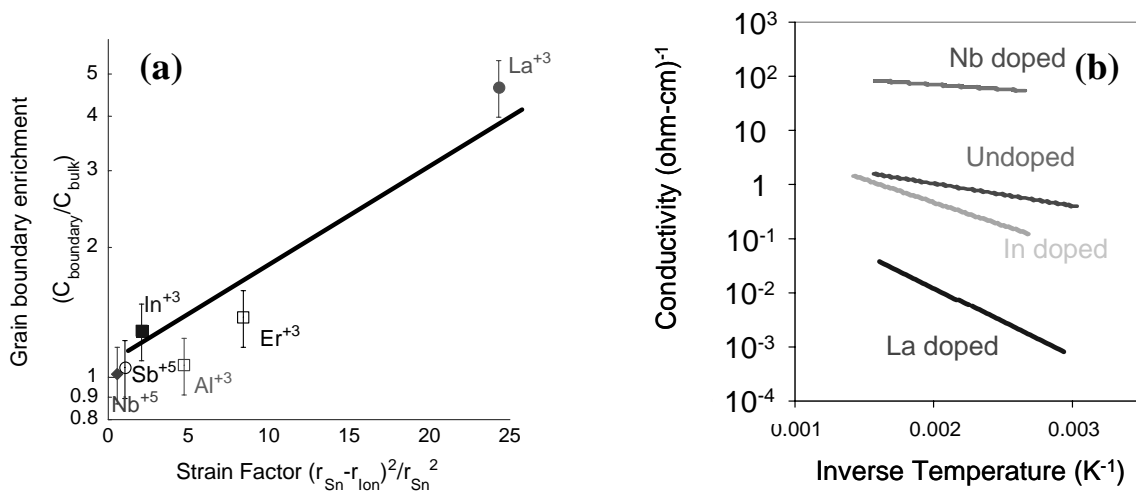


Figure 3 (a) Grain boundary enrichment of dopants as a function of misfit strain factor. (b) Film conductivity as function of temperature for SnO₂ films with different doping types.