Structural properties of thin ZnO films grown by ALD under O-rich and Zn-rich growth conditions and their relationship to electrical parameters

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Motivation

Extensive research efforts are being made worldwide to overcome the obstacles of conductivity control and its conversion towards p-type in wide bandgap semiconductors like ZnO. The success of these efforts will ensure the development of practical technologies e.g., piezo-phototronics, ZnO-based p-n homojunction, thin film transistors. Charged native point defects and Hydrogen impurities were prime suspect of donors in ZnO. recent investigations strongly suggest that hydrogen impurity in ZnO material may be involved in a number of complexes with native point defects, such as V_{Zn}-nH, Zn_i - V_O-H, and others . Some of these complexes introduce shallow donor and acceptor levels that affect the resulting ZnO conductivity. Current investigations aimed to control the conductivity of ZnO-ALD thin films through native and structural defects and their complexes [1]. The former can be tuned via the stoichiometry of the films by changing it from O-to Zn-rich condition [2] and later can be improved via annealing.

Experimental

- Two series of ZnO/Si and ZnO/Al_2O_3 films grown by Atomic Layer Deposition (ALD) technique
- The range of T_g =100 ,130, 160, 200, 250, 300˚C
- Thickness of the films ≅ 100nm
- films are polycrystalline having certain preferred orientations on Si and *a*-Al_2O_3 substrate
- The average crystallites size (*l*) is ~ 20-30 nm and it increases after annealing to 80-90 nm, thus modifies surface roughness as seen in AFM images.

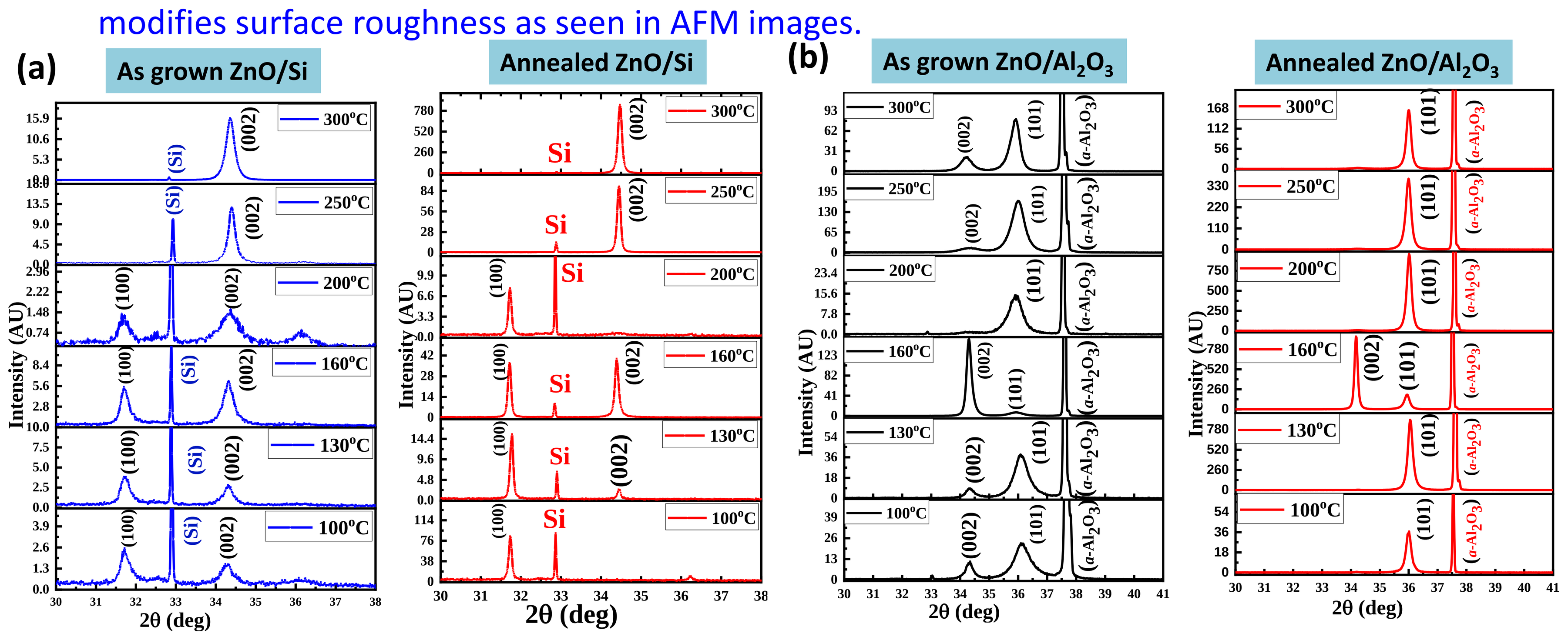

Figure 1. X-ray diffraction pattern of (a) ZnO/Si (b) ZnO/*a*-Al_2O_3 for as grown and annealed films

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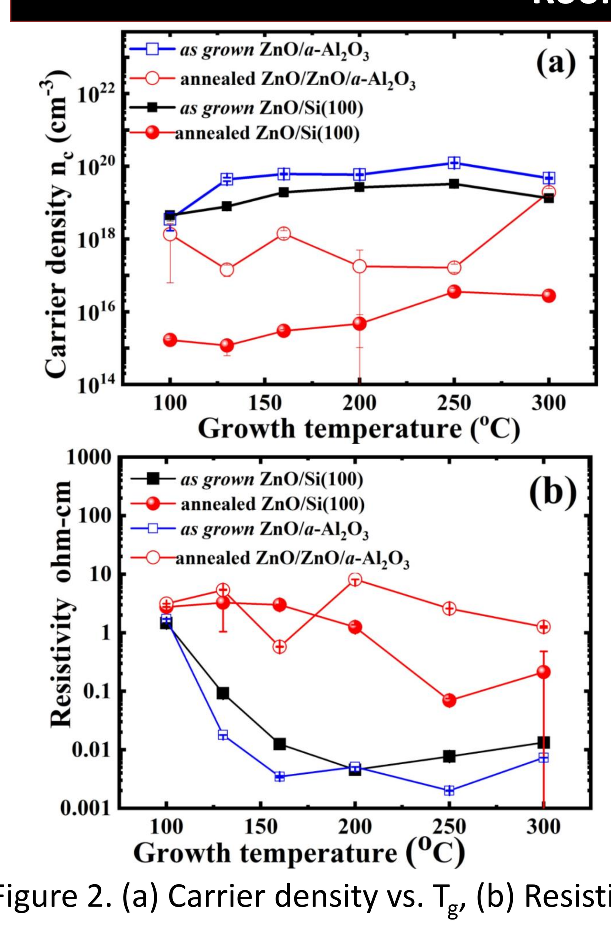
Electrical properties

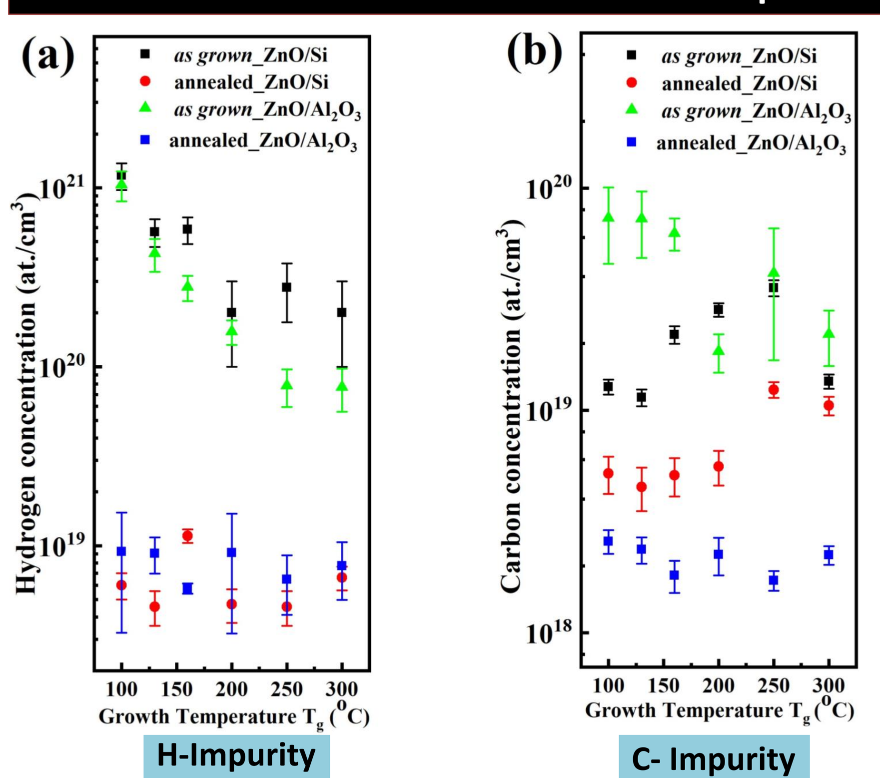
Room temperature Hall measurements



- conductivity of the films increases with successive T_g.
- ZnO/Si films show lower carrier concentration and higher resistivity than those deposited on *a*-Al_2O_3.
- After post growth annealing (O_2 atm, 800 ˚C, 3 min) both for thin ZnO/Si and ZnO/Al_2O_3 films Electron density decreases whereas resistivity increases.
- Calculated Debye length (L_D) was found to be shorter than l/2 (half of crystallite size) for most of the ZnO/Al_2O_3 and ZnO/Si samples and longer for annealed ZnO/Si
- The carrier distribution homogeneity and carrier scattering mode is different for ZnO/Si as compared to ZnO/Al_2O_3.

Figure 2. (a) Carrier density vs. T_g, (b) Resistivity vs. T_g for ZnO/Si and ZnO/*a*-Al_2O_3

SIMS: Impurities incorporation



- Secondary ion mass spectroscopy confirmed, hydrogen impurity concentration in all *as grown* films is ~10^{20-21}/cm³
- The three-minute annealing in oxygen at 800 °C significantly reduced hydrogen and carbon impurities~10^{18-19}/cm³ clearly higher than corresponding electron density (~10^{15-17}/cm³)
- indicating all hydrogen does not participating in conductivity
- Overall electrical parameters of thin ZnO films show a high sensitivity to growth conditions as well as interface.

Figure 3. Hydrogen (a) and carbon (b) concentration in *as grown* (black squares) and annealed (red squares) ZnO /Si films, *as grown* (green triangle) and annealed (blue squares) ZnO/Al_2O_3 grown at different T_g.

AFM: Surface Morphology

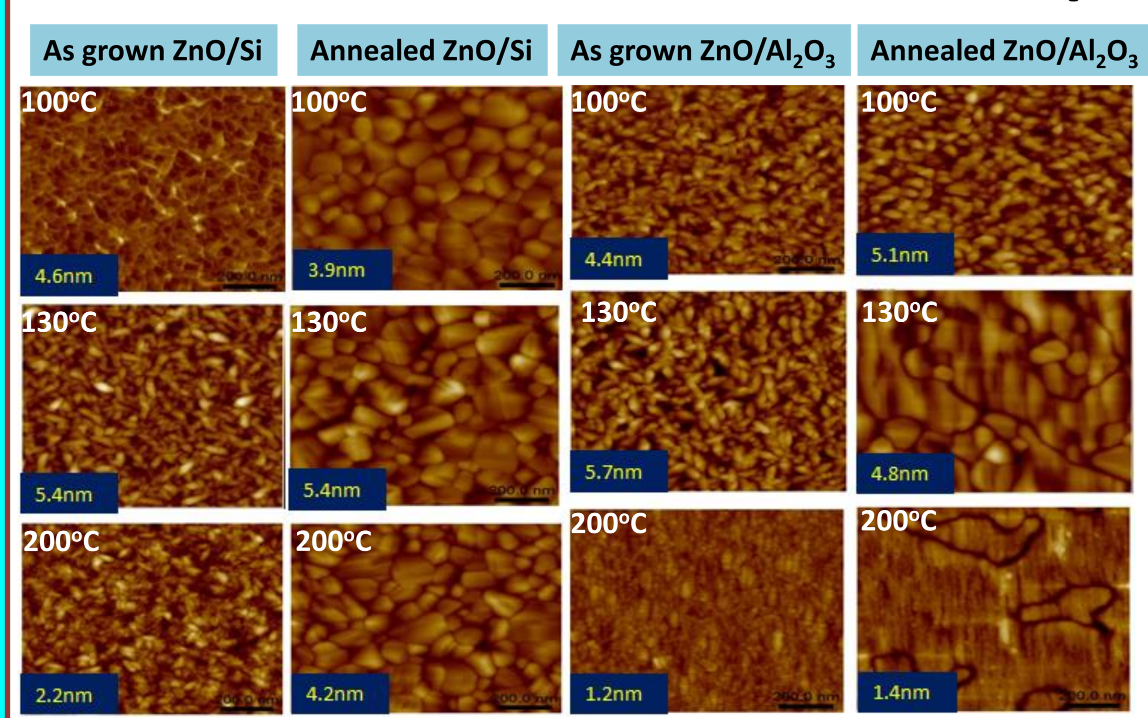
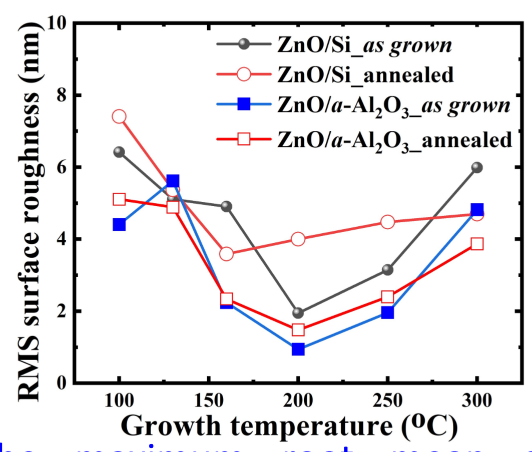


Figure 3. AFM images of *as grown* and annealed thin ALD ZnO/Si films and ZnO/*a*-Al_2O_3 films grown at 100,°C, 130°C and 200°C respectively. The graph of roughness variation with T_g for all types of *as grown*/annealed films has also been shown below the images.



- The maximum root mean square (RMS) value of the surface roughness was found for the films grown at T_g ≅ 100 °C–130 °C
- The RMS value gradually decreases with growth temperature T_g [4].
- The lowest RMS values are observed at 160–200 °C, when switching of crystallographic orientation occurs.

Structural imperfection

Strain, Dislocation density

The films deposited on silicon showed reduced strain and dislocation density compared with the films deposited on sapphire. The three-minute annealing in oxygen at 800 °C significantly improved the quality of all ZnO layers, as evidenced by lower dislocation density as well as reduced hydrogen and carbon impurities.

Tensile strain was observed for as grown ZnO/Si(100) and ZnO/ *a*-Al_2O_3 films, higher for the latter, but its evolution after annealing was different. The strain was reduced in the ZnO/Si(100) films, while it increased in the ZnO/ *a*-Al_2O_3 layers after a short annealing at 800 °C. For the latter films, a good correlation was found between the degree of strain, Urbach energy, and dislocation density as a function of Tg. As expected, Eu was reduced after annealing.

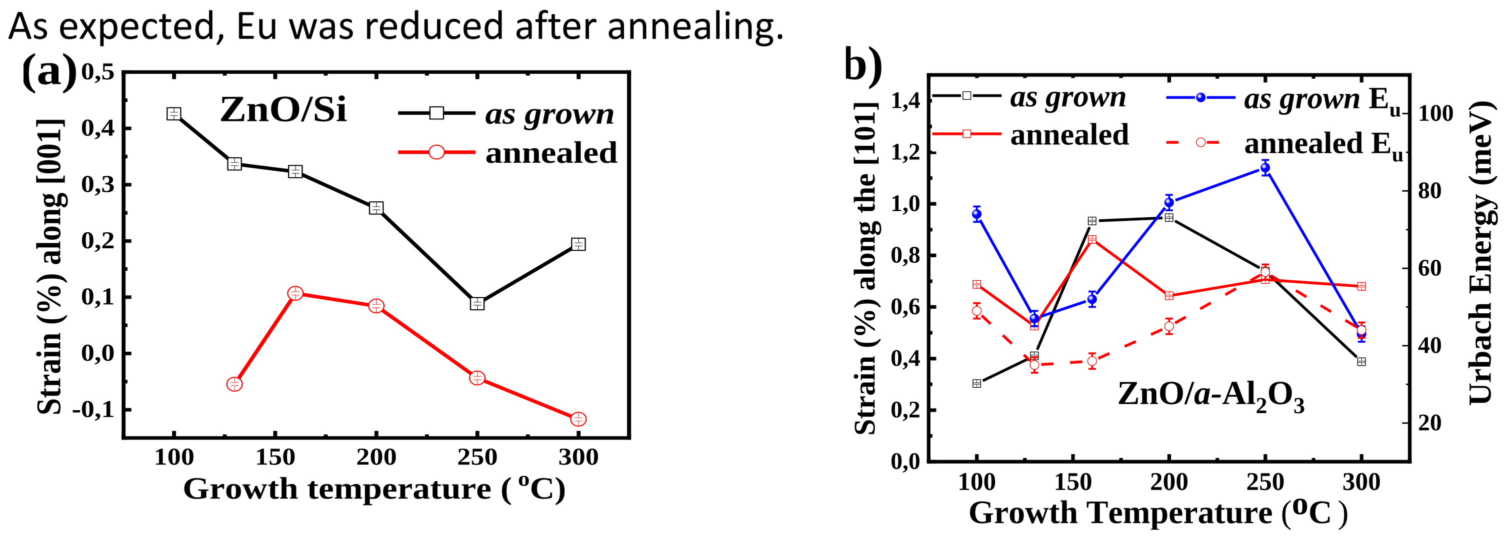


Figure 4. (a) The values of strain along the c ([001]) direction in *as grown* (open square) and annealed (open circle) ZnO/Si films, (b) along the [101] direction in *as grown* and annealed ZnO/*a*-Al_2O_3 films; the star indicates the only layer with the [001] preferred orientation.

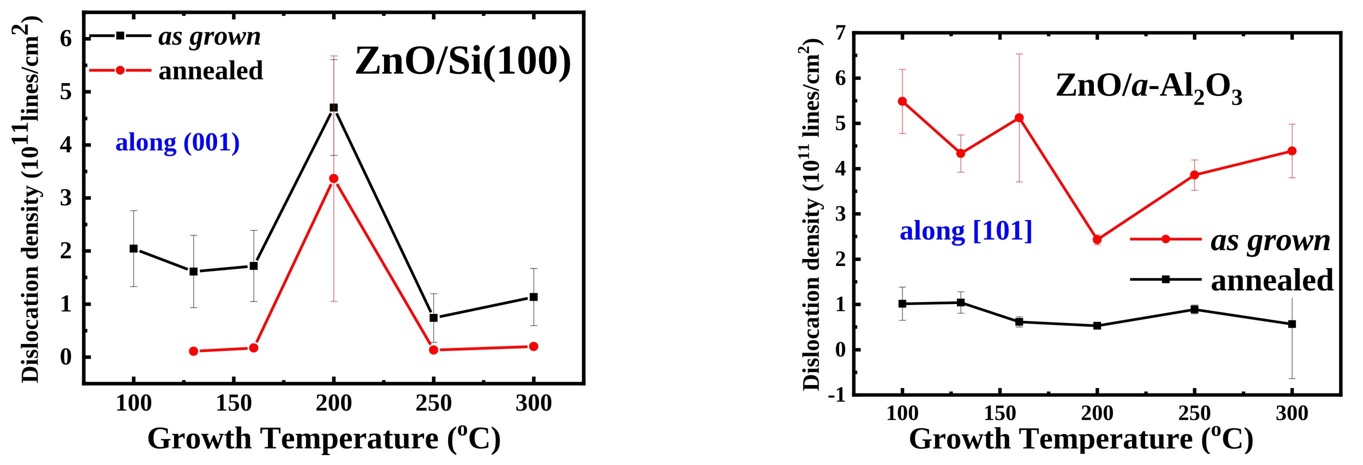


Figure 5. Dislocation density versus Tg for as grown and annealed films (a) along the preferentially oriented [001] crystallites in ZnO/Si films, (b) along the [101] oriented crystallites in ZnO/*a*-Al_2O_3 films.

Conclusions

- Films deposited at lower temperatures, 100–130 ˚C, showed a lower carrier concentration, which was accompanied by a high hydrogen content.
- The uniform carrier distribution envisaged for annealed ZnO/Si(100) films deposited at T_g of 160 ˚C or below (i.e., O-rich), as well as lower dislocation density and strain, predesignated these films for electronic applications, such as field effect transistors or memory devices.
- The level of structural defects also plays an important role, indirectly pointing to their possible role in the formation of hydrogen impurity–native point defect complexes providing shallow defect levels.
- Substrate found to affect dislocation density, strain and electrical transport in polycrystalline ZnO films
- A good correlation was found between the degree of strain, Urbach energy, and dislocation density as a function of T_g. As expected, E_u was reduced after annealing.

References:

[1] S. Mishra et al *Materials.* ***2021*** Jan;14(14):4048.
[2] E. Przezdziecka et al, *Influence of Oxygen-Rich and Zinc-Rich Conditions on Donor and Acceptor States and Conductivity Mechanism of ZnO Films Grown by ALD—Experimental Studies*, J. Appl. Phys. **127**, 075104 (2020)
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