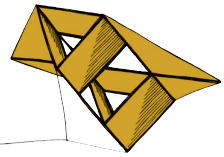

Atom-by-atom growth of ZnO_x films: molecular-dynamics simulations

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1 Introduction

Zinc oxide (ZnO_x) is a technologically important compound crystallising in hexagonal wurtzite structure. The wurtzite (w-) ZnO is a transparent conducting oxide (TCO) with piezoelectric and pyroelectric characteristics. Its properties allow it to be used in a variety of optoelectronic applications, including short-wavelength LEDs, piezoelectric transducers, solar cells, and other devices. For numerous applications, zinc oxide is prepared in the form of thin films, and the largest possible monocrystalline grains are required. For example, the conductivity of w-ZnO_x, especially at the elemental ratio x = [O]/[Zn] near 1, is highly affected by its crystallinity. The more crystalline the material (film) is, the more conductive it is.

The aim of this contribution is to reproduce the atom-by-atom film growth by molecular-dynamics simulations in order to provide quantitative information about the correlations between the zinc oxide characteristics and the growth parameters. This information is used to determine the criteria that lead to the highest quality films. The findings are particularly relevant for ion-assisted deposition techniques such as direct current, radio frequency or high-power impulse magnetron sputtering.

2 Methodology

All simulations were performed by the LAMMPS (Thompson et al. (2022)) software using the Reactive Force Field (ReaxFF) potential (Raymand et al. (2008)).

The value of the x = [O]/[Zn] ratio in the ZnO_x films (not including the template) was set to 0.60, 0.70, 0.80, 0.90, 0.95, 0.97, 1.00, 1.03, 1.05, 1.10, 1.20, 1.30, or 1.40. The fraction of fast atoms (f_{fast}) in the total particle flux (towards the template), which consists of fast atoms with kinetic energy E_{fast} and slow atoms with 0.1 eV, was set to 0, 20, 50, 80, or 100%, and E_{fast} was set to 0.1, 1, 10, or 100 eV. There were two series of simulations, characterised (in parallel to varied x) by (i) varied E_{fast} at f_{fast} = 100%, or (ii) varied f_{fast} at E_{fast} = 10 eV.

Shortest path network ring statistics (Franzblau (1991)) were used to quantify the medium range order and in turn the crystal quality in the films grown by simulations. The comparison of grown structures to w-ZnO was based on the fact that wurtzite contains two rings of length 6 per one atom (R_6 = 2) and no other rings.

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3 Results

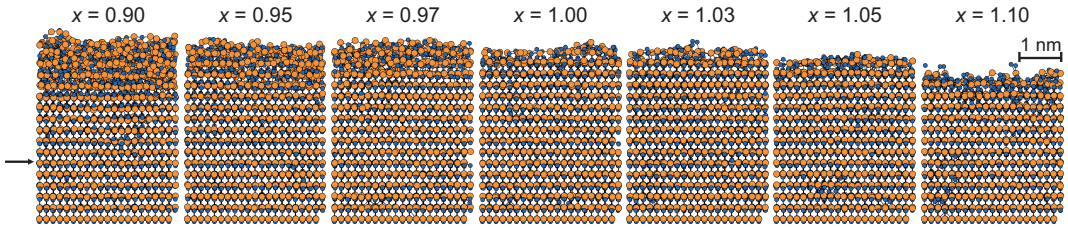

Figure 1: Example of snapshots of ZnO_x structures of various compositions (x = [O]/[Zn]), grown at E_{fast} = 10 eV and f_{fast} = 100%. The arrows point to the interface between the w-ZnO template and the ZnO_x film. Orange balls are Zn atoms and blue balls are O atoms.

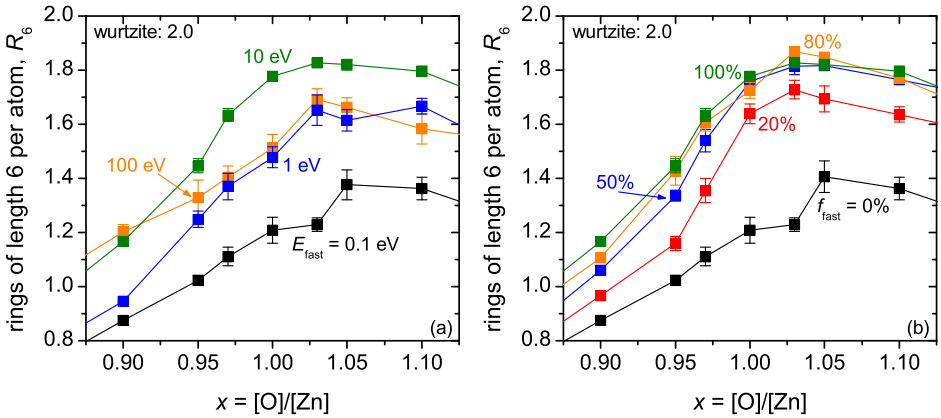

Figure 2: Number of rings of length 6 per one film atom (R_6) dependent on the (a) energy of fast atoms at f_{fast} = 100% and (b) fraction of fast atoms at E_{fast} = 10 eV and E_{slow} = 0.1 eV.

From the ring statistics (Fig. 2(a)) it is possible to see that the crystallinity was improving with increasing x until the value x = 1.03 and then it was slowly deteriorating. Films formed at E_{fast} = 0.1 eV were amorphous (see $R_6 \lesssim 1.4$). The energy of these atoms was not high enough for the films to crystallise. The film with the highest crystallinity was proven to come from atoms with an energy E_{fast} = 10 eV (see Fig. 1) and x = 1.03 (see $R_6 \gtrsim 1.8$). E_{fast} = 100 eV caused higher concentration of defects in the films. Hence, R_6 is lower.

The dependence of R_6 on f_{fast} in Fig. 2(b) shows that R_6 was increasing with increasing f_{fast} and also with increasing x until x = 1.03. The films at f_{fast} = 0% and 100% were the same as those at E_{fast} = 0.1 eV and 10 eV, respectively. The most crystalline films were confirmed for $f_{\text{fast}} \geq 50\%$. It is very important that the most crystalline structures were obtained at the newly identified optimum [O]/[Zn] ratio x = 1.03, not at the intuitive ratio x = 1.00.

References

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