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Nanocrystalline-to-amorphous transition in nanolaminates grown by low
temperature atomic layer deposition and related mechanical properties

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We report on a comprehensive structural and nanoindentation study of nanolaminates of Al2O3 and
ZnO synthesized by atomic layer deposition (ALD). By reducing the bilayer thickness from 50 nm
to below 1 nm, the nanocrystal size could be controlled in the nanolaminate structure. The softer and
more compliant response of the multilayers as compared to the single layers of Al2O3 and ZnO is
attributed to the structural change from nanocrystalline to amorphous at smaller bilayer thicknesses.
It is also shown that ALD is a unique technique for studying the inverse Hall-Petch softening
mechanism (E. Voce and D. Tabor, J. Inst. Metals 79(12), 465 (1951)) related to grain size effects in
nanomaterials. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4711767]

Atomic layer deposition (ALD) is an excellent technique to grow pinhole free, continuous, smooth, and substrate con-
formal thin films with precise dimensional control at the sub-
nanometer level.1,2 The self-limiting surface reactions involved during ALD promote the growth of precise multi-
layered thin films on the substrate.3 The high quality and substrate conformity of films deposited by ALD enables syn-
thesis and surface engineering of complex nanostructures.4,5 Moreover, low-temperature ALD (LT-ALD) within the
range of 25–80 °C allows deposition on temperature-sensitive biological templates5 and flexible polymer sub-
strates,6,7 as well as on temperature sensitive metal oxide surfaces such as Cu2O8 thus opening the route to photovoltaic
and energy-storage devices with innovative architectures.9 In this article, we concentrate on the study of the transition from nanocrystalline to amorphous phases in thin nanolaminates of ZnO/Al2O3 grown by ALD at 65 °C and
their related mechanical properties, hardness and Young’s modulus.

The mechanical behavior of layered and nanocrystal-
line bulk materials has been a topic of extensive investigation.
Several experimental studies have shown that polycrystalline and epitaxial multilayered thin films can be
harder than their constituent components.10 High hardness effects were also observed for nanocomposites11 and for
amorphous metal nanolaminates.12 We report on softening of nanolaminates as a function of the bilayer thickness.
This opens a route to tailor mechanical properties of (transparent conductive) oxide films for specific applications
where mechanical integrity and reliability for opti-
mum electrical and optical performance13 is of utmost
importance during service. We also address fundamental
aspects of the nanolaminates’ mechanical response to
indentation at a nanoscale structural level.

In this study, seven different bilayer thicknesses of
Al2O3/ZnO nanolaminate were investigated ranging from
48 nm to below 1 nm. Single layers of the constituent oxide
compounds were investigated as reference. For experimental
details on synthesis and characterization, see the supplementary
information, Section S3.20 Bilayer thicknesses of the
nanolaminates are summarized in Table I together with indi-
vidual thicknesses of the interlayers and the growth rate per
cycle.

The growth rates of Al2O3 and ZnO in the nanolami-
nates vary between 1.4 to 2 Å per cycle and 1.8 to 2 Å per
cycle, respectively. Multilayer stacks smaller than 0.9 nm
Al2O3/1.6 nm ZnO (bilayer thickness 2.5 nm) were not
measurable on cross sections by scanning He-ion micros-
copy due to resolution limits. Bilayer thicknesses of 1.3 nm
and 0.8 nm represent extrapolated values based on the num-
ber of cycles and measured film thicknesses. Rutherford
backscattering spectrometry (RBS) analysis on 100 nm thick
single ZnO and Al2O3 films grown at 65 °C by ALD
showed that the oxide compounds were stoichiometric.
Elastic recoil detection analysis (ERDA) on Al2O3 showed
a small hydrogen content around 6 at. %, which could be
attributed to a partially hydroxylated phase AlO(OH).7,14
The existence of such a phase is supported by mass spec-
trometry measurements performed on our nanolaminates
showing the existence of an AlH+ fragment in the Al2O3
multilayers.15 However, transmission electron microscopy
(TEM) observations did not show diffraction rings of phases
other than ZnO.

Two illustrative examples of nanolaminates with bilayers thicknesses of 48 nm and 4.8 nm are shown in
Figures 1(a) and 1(b). The high-resolution secondary electron images of cross-sections of the nanolaminates were obtained by breaking the samples prior to observation in a He\(^+\) ion microscope. More cross sectional images of the Al\(_2\)O\(_3\)/ZnO nanolaminates are shown in Figure S1\(^20\) and confirm that the sequence of alternating Al\(_2\)O\(_3\) and ZnO interlayers in the nanolaminate was achieved throughout the total film thickness down to a bilayer thickness of

\[\text{Table I. Summary of low-temperature (65 °C) ALD Al}_2\text{O}_3/ZnO nanolaminate experiments. Exposure cycles, total number of bilayers, resulting thicknesses for the film, the Al}_2\text{O}_3\) and ZnO interlayers, and the bilayers are reported.\]

<table>
<thead>
<tr>
<th>Cycles Al(_2)O(_3)</th>
<th>Cycles ZnO</th>
<th>Number of Bilayers</th>
<th>Film Thickness (nm)</th>
<th>Al(_2)O(_3)</th>
<th>ZnO</th>
<th>Bilayer Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2</td>
<td>400</td>
<td>321</td>
<td>n.m.</td>
<td>n.m.</td>
<td>0.8(^a)</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>200</td>
<td>271</td>
<td>n.m.</td>
<td>n.m.</td>
<td>1.3(^a)</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>100</td>
<td>249</td>
<td>1.6/1.9</td>
<td>0.9/1.7</td>
<td>2.5</td>
</tr>
<tr>
<td>16</td>
<td>10</td>
<td>50</td>
<td>239</td>
<td>2.9/1.8</td>
<td>1.9/1.9</td>
<td>4.8</td>
</tr>
<tr>
<td>38</td>
<td>25</td>
<td>20</td>
<td>246</td>
<td>7.8/2.0</td>
<td>4.4/1.8</td>
<td>12.3</td>
</tr>
<tr>
<td>77</td>
<td>50</td>
<td>10</td>
<td>248</td>
<td>15.2/2.0</td>
<td>9.5/1.8</td>
<td>24.7</td>
</tr>
<tr>
<td>154</td>
<td>100</td>
<td>5</td>
<td>242</td>
<td>28.3/1.8</td>
<td>20.0/2.0</td>
<td>48.3</td>
</tr>
<tr>
<td>1540</td>
<td>—</td>
<td>0</td>
<td>223</td>
<td>1.4</td>
<td>—</td>
<td>single</td>
</tr>
<tr>
<td>—</td>
<td>1000</td>
<td>0</td>
<td>200</td>
<td>—</td>
<td>—</td>
<td>2.0</td>
</tr>
</tbody>
</table>

\(^a\)Note that the bilayer thicknesses of 0.8 nm and 1.3 nm represent extrapolated values, which could not be verified by scanning electron/ion microscopy ("n.m." stands for not measurable).
The functions were found to be independent of the indentation depths used in this study.

The decreasing trend of the reduced elastic modulus of the nanolaminates is attributed to the structural transition from nanocrystalline to amorphous nature of the ZnO interlayers.

The reduction in hardness can be rationalized in the following manner. Since hardness can be directly related to the yield stress $\sigma$ roughly by a factor of $3^{16}$ an analogy can be drawn to the classical Hall-Petch strengthening effect $\sigma \sim k \times d^{-0.5}$ found in polycrystalline metals, $d$ being the grain size and $k$ a constant.$^{17}$ Reducing the grain size makes operation of dislocation-based deformation mechanisms inside the grain volume increasingly difficult, and the Hall-Petch strengthening effect is observed, $H \sim 1/d^n$.

An inverse Hall-Petch like behavior is found for the low-temperature ALD grown ZnO/Al$_2$O$_3$ nanolaminates (Eq. (1)).

Figure 2 shows that the inverse Hall-Petch like regime extends to a bilayer spacing of about 45 nm, where the average hardness and modulus of the constituent ZnO and Al$_2$O$_3$ films is reached. An inverse Hall-Petch relation, $H \sim d^{-m}$, is found in nanocrystalline materials with the exponent $m$ varying from 0.1 to about 1, when the average grain size is below 30 nm.$^{18}$ The reduction in hardness is attributed to a change in deformation mechanism from dislocation-based to grain boundary sliding, which is the primary deformation mode in nanocrystalline ceramics exhibiting plastic deformation at room temperature and super-plasticity at high temperatures.$^{19}$ However, it is important to note that, in this study, softening of the nanolaminates is observed despite the confinement of the nanocrystalline ZnO layers by the amorphous Al$_2$O$_3$ layers. Also, noteworthy is the ability to tune the mechanical properties of the nanolaminates below the range of the mechanical properties of the constituent ZnO and Al$_2$O$_3$ layers.

In summary, this study has illustrated that nanolaminates of Al$_2$O$_3$ and ZnO synthesized by ALD become softer with smaller bilayer spacing due to a structural transition from crystalline to amorphous. The sub-nanometer precision
control of ALD allows accurate assessment of the mechanical properties of nanocrystalline ceramics with grain sizes within the inverse Hall-Petch regime. The ability to tune the mechanical behavior of thin films via controlling the stacking sequence with the precision of single monolayers by ALD should be very useful in the fields of protective coatings and gas diffusion barriers for photovoltaic devices, window coatings, and food packaging.

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20See supplementary material at http://dx.doi.org/10.1063/1.4711767 for more information about the scanning electron and ion microscopy observations, the indentation experiments, and the experimental section details.