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Transition in layer structure of atomic/molecular layer deposited ZnO-zincone multilayers

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In this work, atomic-resolution transmission electron microscopy studies show that in atomic/molecular layer deposited ZnO-zincone [(ZnO)x(Zn-O-C6H4-O)b] multilayer thin films, ZnO crystals grow vertically and continuously through lateral zincone monolayers. When the thickness of zincone is increased from one to few monolayers, the growth of the ZnO crystals becomes confined, leading to the formation of discrete ZnO/zincone interfaces accompanied by a decrease in roughness. Apart from providing understanding on the formation of interfaces and on the structure of hybrid multilayers, these findings are relevant, e.g., for understanding thermoelectric interface phenomena at inorganic-organic interfaces and x-ray reflectometry of hybrid multilayer thin films. Published by the AVS.

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I. INTRODUCTION

Atomic/molecular layer deposited (ALD/MLD) inorganic-organic thin films have recently emerged as interesting candidate materials for applications such as Li-ion batteries and thermoelectrics.1,2 Much of the interest toward the ALD/MLD technique stems from the fact that it allows for combining inorganic and organic constituents in a layer-by-layer fashion with the materials’ growth and interfaces controlled at the level of a monolayer.3–6 The proof-of-the-principle ALD/MLD materials for thermoelectrics are the ZnO-zincone [(ZnO)x(Zn-O-C6H4-O)b] nanoscale multilayers, for which the performance largely relies on phonon scattering at the inorganic-organic interfaces.5,7,8 More than a monolayer of zincone is, however, required for exploitation of the thermal mismatch between ZnO and zincone and diffusive phonon transport over the ZnO-zincone interface.7 This raises a question whether a monolayer of zincone is, in fact, a well-defined layer and if discrete ZnO/zincone interfaces are formed. It is clear on the basis of previous cross-sectional microscopy and x-ray reflectometry (XRR) studies that the deposition of a monolayer of zincone in between thicker ZnO layers leads to the formation of an interlayer with a density lower than that of ZnO.5–12 However, it is not clear whether these low density interlayers are well defined, that is, laterally closed and continuous zincone, and whether the crystalline ZnO layers could be vertically continuous. In situ quartz crystal microbalance and spectroscopic ellipsometry are methods that can be employed for monitoring the ALD/MLD film growth. Although these methods are sensitive enough to observe the deposition of a monolayer, they are indirect in nature. On the other hand, transmission electron microscopy (TEM) is a powerful technique for direct observation of interfaces at monolayer precision; although TEM has been applied to the observation of ALD/MLD multilayers,3,11 the imaging was seldom done at atomic resolution.

In this communication, we show for ZnO-zincone multilayers via high-resolution TEM that the ZnO crystals can grow and be continuous through the interfaces with a monolayer of zincone such that the crystal orientation of ZnO is preserved. It follows that the average cross-plane crystal size of ZnO—unexpectedly but notably—exceeds the multilayer period. The growth mode experiences a transition for thicker organic interfaces, as few monolayers of zincone are found enough to confine the growth of the crystalline ZnO grains between the organic layers.

II. EXPERIMENT

Zincone thin films were grown by MLD using diethyl zinc (ZnEt₂) as the metalorganic precursor and hydroquinone (HQ; HO-C6H₄-OH) as the organic precursor.13 As the process is based on ligand-exchange reactions between the Et groups of ZnEt₂ and the OH groups of HQ, ideally a layer of Zn-O-C₆H₄-O monomer units is deposited by each deposition cycle. The ZnO-zincone multilayers were deposited by combining the zincone process with the common ZnEt₂/H₂O ALD process for ZnO; this is straightforward as both the processes are based on the same ligand-exchange reactions. The deposition was controlled by the (a+b)×c sequence, where a and b are the numbers of deposition cycles for ZnO and zincone, respectively, and c is the number of supercycles; the films were finished with a cycles of ZnO. While a and b are used to control the thickness of the individual layers, c is used to adjust the total thickness of the films. To deposit multilayers with zincone monolayers between thicker ZnO layers, a:b:c parameters 50:1:9 and 10:1:47 were used and are labeled as 50:1 and 10:1. To study the effect of zincone interlayer thickness, cycle numbers of 50:5:7 and 50:9:7 were used; these are denoted as 50:5 and 50:9. All the films had thicknesses in the range of 45–100 nm and were deposited on Si substrates at
150 °C (OpAL reactor, Oxford Instruments); more details on our deposition process can be found elsewhere.\textsuperscript{14}

Fourier transform infrared (FTIR) spectroscopy was used to characterize chemical bonding in the materials (Bruker Tensor 27 spectrometer). X-ray diffractometry (XRD) was applied in symmetric θ/2θ configuration to obtain the crystal structure of the thin films (PANalytical X’pert Pro diffractometer). High angle annular dark field-scanning transmission electron microscopy (HAADF-STEM; probe corrected JEOL ARM 200F, operated at 200 kV) was used for atomic-resolution visualization of film crystallinity and for direct observation of the one-to-few monolayer-thick zincone interfaces. XRR (PANalytical X’pert Pro diffractometer) was employed to corroborate the TEM data. The XRR patterns were fitted for the quantification of layer thickness, density, and roughness; further details on this procedure are provided in the supplementary material.\textsuperscript{17}

III. RESULTS AND DISCUSSION

The FTIR spectrum for the ZnO film showed only the phonon mode at around 400 cm\textsuperscript{-1} (Fig. 1). For the zincone film, three key absorption features were observed. The ones at 1492 and 1204 cm\textsuperscript{-1} correspond to the stretching vibrations of the C=\textsuperscript{2}C double bond and the C—O single bond, respectively, and reveal the presence of the organic units in the film structure. The absorption at 788 cm\textsuperscript{-1} stems from Zn—O vibrations associated with the zincone structure\textsuperscript{10} and confirmed that organic units were linked via O—Zn—O bonds, as suggested by the reaction mechanism for the film growth. The spectra for the multilayer films are a combination of the spectra for ZnO and zincone; for the 50:1 multilayer, only a weak C=\textsuperscript{2}C peak was observed due to the very low organic content in this film. Moreover, XRD patterns showed that the ZnO and the multilayer films exhibited crystallinity ascribed to the wurtzite-structured ZnO, while the zincone film was found amorphous (Fig. S1).\textsuperscript{17}

HAADF-STEM images are shown in Figs. 2 and S2.\textsuperscript{17} In all the images, the light and dark tones stand for high mass density (ZnO) and low density (zincone), respectively. A clear multilayer structure with long-range in-plane uniformity was seen for the 50:1 and the 50:9 multilayers [Figs. S2(a) and S2(b)].\textsuperscript{17} Note that the density profile for the 50:1 sample in principle gives a picture of the well-formed zincone interlayers. However—most interestingly—regardless of the observed multilayer periodicity of around 10 nm [also obtained via XRR (Table S1)],\textsuperscript{17} a higher magnification revealed the presence of large columnar grains with cross-plane grain size up to the full film thickness for the 50:1 multilayer [Fig. 2(a)]. This is in line with the XRD data that also indicated a cross-plane grain size larger than the multilayer period (Table S2).\textsuperscript{17} Hence, monolayer-thick zincone does not stop the growth of the ZnO crystals, and the monolayers can be interpreted as embedded inside the columnar ZnO crystal grains. The observation that the ZnO crystals can grow through the organic monolayers was corroborated by a higher magnification image that illustrates continuous propagation of a ZnO crystal through a zincone monolayer [Fig. 2(b)]. Note that, as for the 50:1 multilayer, also for the 10:1 multilayer, the ZnO crystals were observed to extend over various multilayer periods [Fig. S2(c), Table S2].\textsuperscript{17} When the thickness of the zincone interlayers was increased, they were indeed found to limit the growth of ZnO crystals as is seen in Fig. 2(c) for the 50:9 multilayer. The ZnO layers in the 50:9 multilayer film were fully crystalline, only the orientations of the ZnO crystals were not transferred to the next ZnO layer [Fig. 2(d)]. The different observed growth modes lead to different interface roughness profiles. For the 50:1 multilayer, the interface roughness follows the shape of the growth front of the large columnar ZnO crystal grains such that roughness increases for the first six to seven multilayer periods and then levels off or slightly decreases approaching the film surface [Fig. 2(a)]. For the 50:9 multilayer, the interface roughness does not increase that strongly along with the film thickness, as the growth of the ZnO crystals stops at each zincone interface [Fig. 2(c)].

The XRR pattern for the 50:1 multilayer showed small and large interference fringes ascribed to the total film thickness and the multilayer structure, respectively [Fig. 3(a)]. The small fringes were seen to smooth out above around 1° owing to surface roughness and/or interface roughness. To better understand the role of roughness on the shape of the XRR patterns (prior to fitting), the measured pattern for the 50:1 multilayer was compared to patterns simulated with different roughness profiles [Fig. 3(a)]. It was found out that the smooth out of the small fringes cannot be explained by low overall roughness (i), high surface roughness (ii), or high but constant interface roughness (iii). Instead, it was evident that the XRR pattern with nonconstant roughness (iv) provided the closest resemblance to the data and hence a valid initial guess for the fitting. As the roughness profile for the pattern (iv) was constructed based on the TEM-based roughness profile [Fig. 2(a)], the present TEM-based information was found vital for the otherwise complex XRR fitting procedure (for the fitting procedure see the supplementary material).\textsuperscript{17} As a result of the fitting, average interface roughness values of 2.3, 1.6, and 1.1 nm were obtained for the 50:1, 50:5, and 50:9 multilayer films, respectively; this is in line with the TEM results in that higher interface roughness was seen to

*Fig. 1. Fourier transform infrared spectra for ZnO, zincone, and the multilayer films with various $ab$ ratios.*

build up for the 50:1 multilayer than for the 50:9 multilayer owing to the different growth modes (Fig. 2).

The density values obtained via the XRR fitting for the full-thickness ZnO and zincone films were 5.6 and 1.9 g/cm³, respectively, in line with the shift of the critical angle [Fig. 3(b)], and in good agreement with the values of 5.49 and 1.95 g/cm³ obtained by Rutherford backscattering spectrometry. For the zincone interlayers in the 50:9 multilayer, the density value of 2.0 g/cm³ was obtained from the fit, in good agreement with the value of 1.9 g/cm³ for the full-thickness zincone film. For the 50:9 multilayer, the obtained interlayer thickness of 1.9 nm corresponded to zincone growth of 2.1 Å/cycle, in agreement with the literature values for zincone in the range of 1.5–2.5 Å/cycle. Hence, well-developed and closed zincone interlayers as well as discrete inorganic-organic interfaces were likely present in the 50:9 multilayer; that is, nine zincone cycles provided a complete surface coverage of ZnO surface during the film growth. This conclusion is in line with the TEM results that indicated confinement of the ZnO crystals by the zincone interlayers in the 50:9 multilayer. On the contrary, for the 50:1 and 50:5 multilayers, the high interlayer density values of 4.9 and 3.4 g/cm³ implied intermixing of zincone with ZnO. Furthermore, for the 50:1 and 50:5 multilayers, the obtained interlayer thickness values of 1.8 and 2 nm correspond to the growth of 18 and 4 Å/cycle for the interlayers, respectively. The fact that especially 18 Å/cycle is notably above the 1.5–2.5 Å/cycle expected for zincone suggests that the interlayers must be composed of both zincone and ZnO, that is, for one or five cycles of zincone complete surface coverage of the ZnO surface during the growth is not achieved. Such intermixing seen via XRR is in line with
the TEM results that indicated the growth of the ZnO crystals through the zincone interlayers for the 50:1 multilayer. Note hence that, although the multilayer fringes in the XRR patterns can be rightfully ascribed to the presence of a multilayer structure (i.e., a stack of alternating layers with mutually different densities), these fringes cannot be used as sole and unambiguous evidence for the presence of well-developed zincone interlayers and discrete ZnO-zincone interfaces. The XRR results are compiled in Table S1.17

The HAADF-STEM and XRR results imply that the zincone monolayers may not be closed and continuous layers. This is in line with modeling of the ZnO-zincone interfaces, where marked repulsive forces between the benzene rings have been seen to prevent their bonding to every Zn atom on the ZnO surface.15 Hence, the growth of ZnO chains also have been seen to prevent their bonding to every Zn atom on the ZnO surface.15 Hence, the growth of ZnO chains also could rather be ascribed to defects on the surface of ZnO. In that case, the incomplete surface coverage by benzene rings in the open volumes can even be up to few-nanometers wide and the incomplete surface coverage by benzene rings could rather be ascribed to defects on the surface of ZnO. It could be that such additional growth pathways enable local epitaxylike growth of the ZnO lattice through the monolayer-thick zincone layers. Closure of the zincone layers then takes place upon the deposition of few zincone cycles, which leads to loss of the local epitaxy-like conditions at the ZnO-zincone-ZnO interfaces.

The ZnO-zincone multilayers exhibit low thermal conductivity owing to phonon scattering at the inorganic-organic interfaces. However, more than a monolayer of zincone is required for exploitation of the thermal mismatch between ZnO and zincone and diffusive phonon transport over the interface.7 This can now be better understood on the basis of the present results stating that few monolayers of zincone are needed to form well-defined layers. For zincone monolayers, the intermixed ZnO can provide an additional pathway for thermal transport through the interface. As interface roughness is also known to be one of the key factors for thermal boundary conductance,16 our findings on interface roughness could help to further refine the description of the thermoelectric interface phenomena in the ZnO-zincone multilayers.

IV. SUMMARY AND CONCLUSIONS

Here, we discovered that in ZnO-zincone multilayers, the zincone monolayers are not laterally continuous, while ZnO crystals exhibit vertical “layer-to-layer continuity.” Zincone layers of few-monolayer thickness, on the other hand, were observed to confine the growth of the crystalline ZnO grains between the organic layers. The refined description of the present multilayer structures leads to improved understanding of the growth of ALD/MLD hybrids and is useful for understanding thermal transport across the inorganic-organic interfaces relevant, e.g., for thermoelectrics. The results are, moreover, important for the state-of-the-art XRR diagnostics of the present-kind multilayer thin films.

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17See supplementary material at https://doi.org/10.1116/1.5105348 for XRD data, XRR fitting procedure and data, and TEM images.