1. Introduction

Thin films and nanostructures of the refractory metal oxide MoO$_3$ have received broad attention in the last years [1, 2]. In many studies its great potential for a variety of applications has been revealed, including redox catalysts [3], chemical sensors [4–6], photochromic [7], electrochromic [8, 9], gasochromic [10, 11], memristive and memcapacitive [12], organic light emission devices (OLEDs) [2, 13, 14], organic [15] and amorphous Si [16–18] solar cells as well as micro-batteries [19–21].

In thin films of MoO$_3$ two different crystalline phases have been found: orthorhombic $\alpha$-MoO$_3$, which is the thermodynamically stable compound, and metastable monoclinic $\beta$-MoO$_3$. The building blocks of $\alpha$-MoO$_3$ and $\beta$-MoO$_3$ are highly distorted MoO$_6$ octahedra with bond lengths and bond angles that strongly deviate from the symmetric octahedron. The crystal structure of $\alpha$-MoO$_3$ consists of a sequence of bilayers that are oriented perpendicular to the b-axis (figure 1(a)). Each bilayer consists of two sublayers of closely packed distorted MoO$_6$ octahedra linked within a layer by a corner to the neighboring octahedra (along a) and sharing a common edge with neighboring octahedra of the adjacent plane of the bilayer (along c). Each bilayer mainly interacts with the two adjacent ones through weak van der Waals interactions, resulting in a sheet-like structure similar to graphite. The crystal structure of $\beta$-MoO$_3$ (figure 1(b)) is similar to that of ReO$_3$ [22]. The distorted MoO$_6$ octahedra form a three-dimensional network by sharing the corners with each other with the unit cell containing four MoO$_6$ octahedra.

Interface structure and composition of MoO$_3$/GaAs(001)

Anirban Sarkar$^1$, Tanveer Ashraf$^2$, Wolfgang Grafeneder and Reinhold Koch$^3$

Institut für Halbleiter- und Festkörperphysik, Johannes Kepler Universität Linz, Altenberger Straße 69, 4040 Linz, Austria

E-mail: reinhold.koch@jku.at

Received 20 December 2017, revised 15 February 2018
Accepted for publication 2 March 2018
Published 19 March 2018

Abstract

We studied growth, structure, stress, oxidation state as well as surface and interface structure and composition of thermally-evaporated thin MoO$_3$ films on the technologically important III/V-semiconductor substrate GaAs(001). The MoO$_3$ films grow with Mo in the 6+ oxidation state. The electrical resistance is tunable by the oxygen partial pressure during deposition from transparent insulating to semi-transparent halfmetallic. In the investigated growth temperature range (room temperature to 200 °C) no diffraction spots are detected by x-ray diffraction. However, high resolution transmission electron microscopy reveals the formation of MoO$_3$ nanocrystal grains with diameters of 5–8 nm. At the interface a $\approx$3 nm-thick intermediate layer has formed, where the single-crystal lattice of GaAs gradually transforms to the nanocrystalline MoO$_3$ structure. This interpretation is corroborated by our in situ and real-time stress measurements evidencing a two-stage growth process as well as by elemental interface analysis revealing coexistence of Ga, As, Mo, and oxygen in a intermediate layer of 3–4 nm.

Keywords: MoO$_3$, GaAs, structure, stress, interface, interdiffusion

(Some figures may appear in colour only in the online journal)
Stoichiometric MoO$_3$ is an insulator with a band gap of $\sim 3$ eV, an electron affinity of 6.7 eV and an extraordinarily large ionization energy of 9.7 eV. On the contrary, oxygen deficient MoO$_3$ with $x < 3$ is an (almost transparent) $n$-type conductor. Because of its large ionization energy the condensation of MoO$_3$ lies close-in-energy to the valence band of organic films and semiconductors (e.g. Si or GaAs).

Accordingly, thin intermediate layers of MoO$_3$ facilitate hole injection into organic films of OLEDs [2, 13–15] and, as discovered very recently, electron extraction in solar cells of amorphous Si [16–18].

Thin films of MoO$_3$ have been prepared by various techniques including thermal evaporation [7, 23–27], sputtering [10, 28–31], pulsed laser deposition [32–34], chemical vapor deposition [35, 36], atomic layer deposition [37], electrodeposition [11, 38], and spray pyrolysis [39], all experiments preferentially performed on amorphous glass or oxidized Si templates. Irrespective of the preparation techniques the following common behavior concerning the dependence on the growth temperature ($T_G$) is observed (see, e.g. [27, 28]): (i) at $T_G < 150^\circ$C amorphous MoO$_3$ are obtained; (ii) at $200 < T_G < 350^\circ$C, the films are polycrystalline with coexisting grains of $\alpha$-MoO$_3$ and $\beta$-MoO$_3$; (iii) for $T_G > 350^\circ$C, XRD reveals only diffraction peaks of polycrystalline $\alpha$-MoO$_3$; (iv) for $T_G > 400^\circ$C, XRD shows only peaks from $\alpha$-MoO$_3$ with the (0 1 0) plane parallel to the substrate yielding textured [28] or epitaxial films [27]; (v) for $T_G > 400^\circ$C, the film thickness is substantially reduced by re-evaporation from surface. In principle, the same sequence of structural transformations is observed, when originally amorphous MoO$_3$ films are annealed at elevated temperatures (see [38]).

Here we investigate growth, structure, oxidation state, stress, interface composition and electrical properties of MoO$_3$ films on GaAs(001), the leading III/V compound-semiconductor. Due to the low effective mass of its carriers, GaAs exhibits superior electronic properties essential for high-speed and radio-frequency devices. Moreover, GaAs is a direct-bandgap semiconductor, thus being perfectly suited for efficient absorbance and emission of light. The latter is utilized in GaAs-based light emitting and laser diodes for CD players, telecommunication [40], and more recently also for lighting LEDs [41]. GaAs solar cells are commonly used for photovoltaic arrays of satellites and hold the world record for the highest-efficiency single-junction solar cell at 28.8 percent [42]. Therefore integration of MoO$_3$ into GaAs(001) technology offers promising prospects for advancing device technology: (i) improved GaAs-based solar cells due to the high ionization energy of MoO$_3$; (ii) tunable electrical resistance from insulating to half-metallic, while maintaining transparency; (iii) epitaxial MoO$_3$ layers due to good lattice matching along $a$ and $c$ in $\alpha$-MoO$_3$ or along $b$ and $c$ in $\beta$-MoO$_3$; (iv) a versatile high-$k$ oxide [43]; (v) possible intercalation into $\alpha$-MoO$_3$.

2. Experimental

The experiments were performed in a multichamber molecular beam epitaxy (MBE) system consisting of separate interconnected growth chambers for III/V semiconductor and metal/oxide MBE. The MoO$_3$ films were deposited onto c(4 × 4) reconstructed GaAs(001) substrates mounted on a cantilever-beam device. They were prepared in the III/V growth chamber by standard routine (for details see [44]). The c(4 × 4) reconstruction of GaAs(001) was confirmed by reflection high energy electron diffraction (RHEED) in the III/V chamber and, after transfer to the As-free metal/oxide chamber without breaking the ultrahigh vacuum conditions, by low energy electron diffraction (LEED) [44]. The MoO$_3$ films were prepared by thermal evaporation of MoO$_3$ powder out of a Mo crucible within 45 min after the sample transfer; the pressure during deposition was $5 \times 10^{-10}$ mbar, the deposition rate was 0.06–0.08 nm s$^{-1}$ as controlled by a quartz crystal microbalance (QCM) calibrated by a QCM in substrate position. The MoO$_3$ films were deposited at different substrate temperatures (room temperature (RT)—200 °C) with and without dosing oxygen via a leak valve. A cantilever beam device [45] was used for measuring the stress of the MoO$_3$ films in real time during growth.

After exposure to air, selected samples were investigated by x-ray diffraction (XRD) with a Seifert XRD3003 (Cu K$_{\alpha} = 0.15418$ nm), by x-ray photoelectron spectroscopy (XPS) with a Theta Probe from ThermoFisher (energy calibration with the 285 eV peak of C, corroborated by XPS peaks of the GaAs substrate), and by atomic force microscopy (AFM) with a nanoSurf AFM in the constant-force contact mode. The electrical measurements were performed in the van der Pauw geometry. From selected samples cross-sectional specimens were prepared by focused ion-beam (FIB) lithography and investigated by high-resolution transmission electron microscopy (HRTEM, JEOL-2011 TEM, 200kV). For chemical analysis cross-sectional specimens were investigated by a JEOL JEM-2200FS (200 kV), which is equipped with a field-emission gun, enabling operation in a scanning mode (STEM), and a silicon drift detector (X-MaxN 80 T from Oxford Instruments) for energy dispersive x-ray spectroscopy (EDXS). Prior to the EDXS-measurements the specimens were oriented into the GaAs[110] zone axis and specimen drift was corrected before each measuring point of a EDXS linescan. To guarantee appropriate resolution and sufficient beam current, a STEM full-width-at-half-maximum beam size $\approx 0.2$ nm was chosen. For the estimated specimen thickness of $\approx 50$ nm the electron beam spread is negligible.
(with only 1% of the electrons being outside of the nominal beam diameter in GaAs), leading to an overall measurement resolution of 0.5 nm.

3. Results

We have investigated the growth of MoO$_3$ on GaAs(001) in the growth temperature range of RT—200 °C and present the obtained results exemplarily by means of MoO$_3$ films deposited at RT and 200 °C. For this study we selected substrate temperatures not higher than 200 °C in order to reduce diffusion of Ga and As into the MoO$_3$ film. In a recent study of Fe/MgO(001)/GaAs(001) heterostructures [46, 47] we found that for growth temperatures of 200 °C a MgO(001) barrier-layer with a thickness of at least 2.5 nm is required in order to suppress interdiffusion of Ga and As into the Fe film as well as of Fe into the GaAs substrate.

3.1. Electrical resistance

Measurements of the electrical resistance by the Van der Pauw method revealed that in order to obtain insulating MoO$_3$ films, a partial pressure of $1 \times 10^{-6}$ mbar oxygen during deposition is required. MoO$_3$ films deposited without oxygen dosage were conducting with a resistivity $\rho \approx 5 \times 10^{-7}$ Ωm at RT, irrespective of the growth temperature. As discussed by Balendhran et al [26], a Mo$^{6+}$ ion neighboring an oxygen vacancy in the MoO$_3$ lattice is reduced to Mo$^{5+}$. The additional electron it is not tightly bound to any Mo$^{6+}$ core cation, thus being delocalized and giving rise to a gap state in between the valence and conduction bands of MoO$_3$. By dosing oxygen during the MoO$_3$ deposition, the number of oxygen vacancies is reduced, eventually leading to insulating MoO$_3$ films.

3.2. Oxidation state

XPS investigation of selected samples showed a Mo 3d$_{5/2}$ peak at 235.9 and 3d$_{3/2}$ at 232.8 eV (figure 2(a)). As discussed in [2], owing to a possible Fermi level shift within the band gap of molybdenum oxides the energy separation between the Mo and O core levels has to be measured as well in order to unambiguously determine the Mo oxidation state. For our films the O 1s peak lies at 530.9 eV (figure 2(b)), yielding an energy separation to the Mo 3d$_{5/2}$ peak of 298.1 eV. This value is in very good agreement with that of Mo$^{6+}$ (297.8 eV) [2]—compared to 299.1 and 300.9 eV for Mo$^{5+}$ and Mo$^{4+}$, respectively [2]—thus confirming the formation of MoO$_3$. The small shoulder on the right side of the oxygen peak (at $\approx$532.5 eV)—contributing only a few percent of the total oxygen signal—is from oxide impurities formed during the transport of the film to the XPS system [2].

3.3. Stress

Figure 3 summarizes the results of the in situ stress measurements. The force $F$ normalized to unit film width $w$ measured during the growth of two MoO$_3$ films on GaAs(001)(4 $\times$ 4) is plotted as a function of the mean film thickness $t$; the slope of the force curves corresponds to the incremental film stress $\sigma = \partial(F/w)/\partial t$. Due to the close correlation between stress and structure, measurements of the film stress have proven to be a powerful tool for investigating film growth as a function of the deposition parameters [48, 49]. Moreover, since the stress measurements are performed in real-time, important information on the dynamics of the growth process is provided [50, 51]. From the force curves of the two MoO$_3$ films deposited at RT and 200 °C (figure 3, left) two different growth stages can be distinguished: (i) a growth stage with large compressive film stress of $-1.1$ GPa at the beginning of deposition up to a thickness of 0.7 nm for the RT film and 1.6 nm for the 200 °C film (linearly increasing film forces correspond to constant incremental film stress $\sigma = \partial(F/w)/\partial t$); (ii) a growth stage with constant lower compressive stress of $-0.3$ GPa for both films at thicknesses larger than $\approx$2 nm. Interestingly, the transition from growth stage (i) to growth stage (ii) proceeds rather sharp at a thickness of 1.7 nm for the RT MoO$_3$ film and smooth for the 200 °C film (see section 4). No change in the film-forces with time is observed after the deposition is stopped; this is shown exemplarily in figure 3, right, which displays the time-dependence of the film forces measured immediately after stopping deposition. As discussed previously [48, 52], constant stress after film deposition indicates that no relaxation processes take place in the deposited films.

3.4. Film structure

We did not observe diffraction spots of $\alpha$-MoO$_3$ or $\beta$-MoO$_3$ in the XRD pattern of our films (figures 4(a) and (b)) apparently
suggesting the growth of amorphous films up to $T_G = 200^\circ C$. Figures 4(c) and (d) show representative cross-sectional overview TEM images of respective MoO$_3$ films deposited at (c) RT and (d) 200 $^\circ$C; red arrows indicate MoO$_3$/GaAs(001) interface.

(see below) Figures 4(c) and (d) show representative cross-sectional overview TEM images of two 30 nm-thick MoO$_3$ films deposited onto GaAs(001)$_c$(4 × 4) at RT and 200 $^\circ$C, respectively. The two films exhibit a nearly identical microstructure resembling the morphology of amorphous films. A similar morphology is reported in the literature for the amorphous phase of MoO$_3$ films prepared by various deposition techniques (e.g. [27, 28, 31] and [38]) at growth temperatures between RT and 200 $^\circ$C. Notice the horizontal stripe, visible in both images (red arrows), with a thickness of about 2–3 nm and clearly distinguishable by its contrast, which lies at the interface between MoO$_3$ and GaAs(001).

Figures 5(a) and (b) display TEM images of the two films at higher magnification. All over in these HRTEM images short rows with lengths of a few nanometer and different orientations. Frequently the rows have arranged to small groups of parallel rows, e.g. marked by red circle in figure 5(a). In reality, these rows represent tiny planes of MoO$_6$ octahedra, frequently aggregated to small nanocrystals with different crystallographic structures and orientations. The red dashed squares in figures 5(a) and (b) mark regions where larger crystalline grains with dimensions of 5–8 nm have formed. Such grains give rise to discrete spots in diffractograms calculated by fast Fourier transformation (FFT) of the respective HRTEM sections. Figures 5(c) and (d) display FFT diffractograms derived from the areas marked by red squares in figures 5(a) and (b), respectively. For comparison, we also show a FFT diffractogram calculated from a pure GaAs region (figure 5(e)). As expected, the resulting diffraction spots form a rectangular array (shown in red) with an aspect ratio of $\sqrt{2} : 1$ (notice that in the cross-sectional TEM samples the GaAs(110) plane is...
parallel to the surface). Whereas the GaAs substrate is a single crystal, the MoO3 region consists of many different and randomly oriented nanoclusters, typically with sizes of 1–2 nm, sometimes even reaching 5–8 nm. Accordingly, spots in FFT diffractograms of the MoO3 region originate from electron diffraction at different crystal planes leading to a complex diffraction pattern with ring-like features as well as discrete spots (see figures 5(c) and (d)). From the FFT diffractograms as well as directly from the HRTEM images—both calibrated via the GaAs lattice—feature spacings of 0.2, 0.25, 0.32, 0.43, or 0.45 nm are observed. Similar spacings are found in the crystal lattices of α-MoO3 (ICPDS card, No. 05-0508) and β-MoO3 (ICPDS card, No. 47–1320). For instance, the Mo–Mo distance in the monoclinic β-MoO3 is 0.27, 0.28, and 0.35 nm along the three different crystal axes; for α-MoO3 the Mo separation along the a and c direction is 0.2 and 0.4 nm, respectively.

Despite the presence of nanoscale order and the formation of nanocrystalline grains no diffraction spots of MoO3 are detected by XRD with our samples (figure 4). This is indeed surprising, because x-ray powder diffraction is a well established technique and XRD is also successfully employed for structural investigations of (typically ordered) nanocrystal arrays. It seems that in the case of MoO3/GaAs(0 0 1) the XRD intensity is weakened by the combined effect of a number of factors: (i) Compared to common powder diffraction experiments the average grain size in our nanocrystalline MoO3 films is more than 2 orders of magnitude smaller (1–10 μm compared to 2–8 nm). Moreover, the observed nanocrystals amount only to a small part of the MoO3 film. (ii) Compared to ordered nanocrystal arrays the nanocrystalline grains of our MoO3 films are randomly oriented, thus reducing the number of scatterers contributing to the intensity a given XRD peak. (iii) The lattice distance of MoO3 is considerably larger than that of metallic nanocrystals, again effectively reducing the number of involved scatterers. (iv) Due to the many defects, being responsible for local strain and variation of interatomic distances, constructive interference is reduced. Altogether, this may explain why the absence of diffraction spots in XRD does not necessarily indicate amorphous growth.

3.5. Surface structure

The interface to the vacuum, investigated by AFM, is characterized by a slightly corrugated surface with a mean roughness of 2–3 nm (figures 6(a) and (b)). In situ structural investigations of the 30 nm-thick MoO3 films by RHEED show diffraction patterns with discrete spots (figures 6(d) and (e)), indicating a crystalline surface structure. Comparison of the RHEED patterns of the MoO3 films deposited at RT and 200 °C with that of the GaAs(001) c(4 × 4) substrate (figure 6(c)) reveals a similar characteristic distance (dashed lines in figures 6(c)–(e)). RHEED is a well established technique for investigating nanostructures, e.g. of semiconductor quantum dots [53]. For our MoO3 samples, in situ RHEED therefore corroborates a slight 3D corrugation of the MoO3 surface in accordance with AFM results (figures 6(a) and (b)). Moreover, and in agreement with our HRTEM results, RHEED confirms that the MoO3 films on GaAs(001) are crystalline on a nanoscopic scale, i.e. both in the bulk and at the surface.

The spatial dimensions of the surface corrugation detected by AFM ranges from 0.2–0.5 μm for the RT film and from 1–3 μm for the 200 °C film. Large-scale (>1 μm) cross-sectional TEM images of both films (not shown) exhibit uniform contrast analogous to figure 4, thus not evidencing the presence of grain-boundaries. Accordingly, the observed surface roughness is not the result of columnar-grain growth or Volmer–Weber growth. Film growth seems to proceed in a layer-by-layer-like manner accompanied by kinetic surface roughening that increases with the growth temperature.

3.6. Interface structure

Similar to the surface of the MoO3 films, also the interface of the MoO3 films to the GaAs(001) substrate is rather sharp. As revealed by HRTEM (figures 5(a) and (b)), for both growth temperatures (RT and 200 °C) the transition from the regular GaAs crystal lattice to the microstructure of the MoO3-films proceeds within a thickness range of 2–3 nm; furthermore, the microstructure of the two MoO3 films is similar. The HRTEM images of figure 7 illustrate the structural changes at the interface with higher resolution: figure 7(a) is focused on the GaAs lattice, figure 7(b) on the MoO3 film structure. We want to emphasize that our HRTEM experiment, i.e. non-aberration-corrected TEM and 50 nm-thick cross-sectional sample of a nanocrystalline MoO3 film, cannot provide detailed information on interface structure and chemical composition with atomic resolution. For instance, observed features in the GaAs sample cannot be attributed to As or Ga or both which, however, is not relevant for the main conclusions of our study.

Figure 6. 4 × 2 μm² AFM image of MoO3/GaAs(001)c(4 × 4) deposited (a) at RT and (b) at T0 = 200 °C; linescan positions marked by arrow. RHEED patterns of (c) GaAs(001)c(4 × 4) and 30 nm-thick MoO3 films deposited at (d) RT and (e) 200 °C onto GaAs(001)c(4 × 4); dashed lines are guides to the eye for illustrating same lattice spacing.
Nevertheless, it is possible to identify structural features typical of (i) the GaAs substrate, particularly its unit lattice marked by red circles in figure 7, and (ii) the MoO$_3$ film with its row-like features discussed above by means of figure 5, marked by green dashed lines in figure 7(b).

Upon approaching the interface from the GaAs side, i.e. from bottom to top of figure 7, the centered rectangular structure of GaAs lattice (indicated by red circles) visible in the HRTEM images at first becomes distorted (first blue arrow). Then the GaAs lattice becomes fractured by row-type features typical of the MoO$_3$ film (green dashed lines and second blue arrow). Finally, after a thickness beyond 2–3 nm, the MoO$_3$ film structure becomes the dominating one (indicated by third blue arrow).

### 3.7. Interface composition

In figure 8 we present STEM-EDXS results from the MoO$_3$/GaAs(001) interface which help to understand the observed structural changes. The electron beam with an average spot size of 0.2–0.3 nm is scanned along the straight lines (yellow) included in the respective STEM images of figures 8(a) and (b). In the diagrams below the distance-dependent element-resolved EDXS-signal is plotted for the four involved components, As, Ga, Mo, and O. Figure 8 evidences that in an 3–4 nm-thick interface region the four elements coexist indicating a considerable intermixing region within this thickness range. Notice that the EDX spectra were measured ex situ, a long time after the film deposition has been performed. Therefore the EDXS spectra do not reflect a time scale. Part of the interface composition originates from intermixing via surface diffusion during deposition of the first MoO$_3$ layers, another part may proceed by bulk diffusion taking place during the further deposition process, and maybe bulk diffusion is going on even after film deposition is finished.

According to figure 8, the concentration of As decreases exponentially to zero within a distance of 3–4 nm at both growth temperatures (dashed line 2). The decay of the Ga signal, on the other hand, extends over a thickness of about 10 nm and sets in approximately 4 nm before the As decay (dashed line 1). As indicated by the peak of the Ga signal at ≈11.5 nm, Ga accumulates at the interface region, where the Mo concentration increases (dashed line 3). The Mo signal reaches its maximum value over a thickness range of 3–4 nm (between dashed lines 3 and 4), where Ga is present as well. Oxygen can be detected also in the GaAs matrix of the interface layer (beginning at dashed line 1) and reaches its maximum value before the Mo signal saturates. It seems that oxygen is reacting also with Ga and As. Interestingly, the EDXS results are very similar for both growth temperatures, indicating a high mobility of all four involved species already at RT.
4. Summarizing discussion

We investigated growth, structure, oxidation state, stress, interface composition and electrical properties of thin MoO₃ films on the single-crystal GaAs(001) substrate. Contrary to previous studies performed on amorphous or polycrystalline templates, where according to XRD amorphous films have been obtained at growth temperatures up to 200 °C, our \textit{in situ} RHEED and \textit{ex situ} HRTEM results clearly evidence the formation of nanocrystalline grains with an average grain size up to about 8 nm. We remark that recently nanocrystalline grains have also been detected in one of the very rare cross-sectional HRTEM investigations of sputtered MoO₃ films [31]. Surprisingly, these sputtered films on an amorphous substrate exhibit a very similar microstructure as our thermally evaporated films on a single-crystal substrate. Our results indicate that experimental verification of nanocrystallinity by XRD is not a straightforward procedure.

The interface of MoO₃/GaAs(001) is not atomically sharp. STEM/EDXS reveals that As, Ga, Mo, and O are coexisting in a thickness range of 3–4 nm. Furthermore, oxygen is detected also in a ≈6 nm thick layer of the GaAs substrate at the interface towards the MoO₃ film. Our HRTEM images suggest that the transition from the GaAs single-crystal lattice to the nanocrystalline structure of MoO₃ proceeds gradually over a thickness range of 3–4 nm. Coming from the GaAs side, at first a 1–2 nm thick interface region has formed, where the GaAs lattice is distorted by interdiffusion. According to STEM/EDXS, Ga is enriched in this layer possibly due to chemical reaction with oxygen. It is continued by a 1–2 nm thick more strongly interdiffused layer in the MoO₃ film that that contains already row-like structures typical of MoO₃.

These results are supplemented by our \textit{real-time} stress measurements that evidence a two-stage growth mode, each of them clearly distinguished by its stress. In the first growth stage, at the beginning of deposition, the interface is formed, which consists of a ≈2 nm-thick intermediate layer, where the four components of the two involved materials (Ga/As and Mo/O) coexist. The experimental stress in this layer is compressive with a magnitude of about 1 GPa. As indicated by our HRTEM results (figure 7(a)), in this growth stage the interface layer seems to be represented by a distorted GaAs lattice with Mo and O on interstitial sites giving rise to compressive stress. The stress in this growth stage can be estimated with the high elastic constant of GaAs ($c_{11} = 119$ GPa) corresponding to strain of $\epsilon \approx 1\%$ due to interdiffusion. Once the nanocrystalline MoO₃ structure is dominating at a film thickness $> 2$ nm, the compressive stress is reduced. The observed stress values of about $-0.3$ GPa are in agreement with the growth stress reported by Mohamed \textit{et al} for sputtered MoO₂ films [54]. In this (second) growth stage each MoO₃ layer adds the same magnitude of force to the film resulting in a linear increase of the film force, corresponding to constant stress. Film growth in the second stage therefore proceeds in a layer-by-layer-like manner. We remark that the observed stress evolution is in clear contrast to that of Volmer–Weber growth (see [48, 49]) in agreement with the observed featureless large-scale TEM images.

We want to emphasize that stress measurements represent a real-time investigation technique providing \textit{in situ} information on structural processes directly during film deposition. The stress results suggest that interdiffusion effects dominate particularly during the process of interface formation, i.e. while depositing the first 1–2 nm of MoO₃. Upon further deposition, interdiffusion continues, though to a lower extent. This is confirmed by our EDXS results performed \textit{ex situ} that reveal an interface layer as thick as 3–4 nm. Interestingly, the transition between the two growth stages identified by the stress measurements is shifted to lower film thickness for the 200 °C film pointing to improved temperature-driven strain relaxation.

According to HRTEM, the MoO₃ film consists of MoO₆-octahedra locally connected via corners and/or edges to neighboring ones forming randomly oriented nanoscale regions of $\alpha$-MoO₃ and $\beta$-MoO₂. Most of these nanocrystalline regions are smaller than 2 nm, only occasionally nanocrystal sizes of 5–8 nm are reached (figure 5). The stress change at the transition between growth stage (i) and growth stage (ii) is rather sharp, occuring at a smaller film thickness at $T_G = 200$ °C. According to figure 5(b) the transition seems to proceed more smoothly at 200 °C. For comparison, the quantitative amount and thickness dependence of interdiffusion, as detected by STEM/EDXS, is (nearly) independent of the growth temperature up to 200 °C.

According to XPS, the oxidation state of the MoO₃ films on GaAs(001) is Mo$^{6+}$. These findings are corroborated by the Mo/O composition ratio of 1:3 determined by STEM/EDXS. The electrical resistance of MoO₃/GaAs(001) can be tuned by the oxygen partial pressure between electrically insulating to electrically conducting like a halfmetal. Whereas the MoO₃ films are transparent in the insulating state, then attain more and more a bluish color with increasing metallic behavior.

All in all, the structure of the presented MoO₃ films on the technologically important GaAs(001) templates as well as their physical and chemical properties are very promising for application of MoO₃ films in future GaAs-based electronic devices. Examples are solar cells with even higher efficiency, magnetoresistive elements for spintronics with MoO₃ tunnel barriers, etc.

Acknowledgments

We thank Jörg Winkler and Harald Köstenbauer from Plansee SE as well as Christian Mitterer (Montan-University Leoben), Alberta Bonanni, Aitana Tarazaga and Heiko Groiss (Johannes Kepler University Linz) for stimulating discussions. We thank Jiri Duchoslav (Johannes Kepler University Linz) for the XPS measurements. We gratefully acknowledge funding by the Austrian Science Fund (FWF), project P24335, and by the Austrian Research Promotion Agency (FFG), project E2Sputtertech. One of us (TA) was funded by a scholarship Austrian Agency for International Mobility (Ernst Mach Follow Up Grant). We also thank National Institute of Lasers and Optronics (NILOP) Islamabad, Pakistan for their cooperation.
Conflict of interest

There are no conflicts to declare.

ORCID iDs

Reinhold Koch https://orcid.org/0000-0001-8194-8191

References

[1] Meyer J, Hamwi S, Kröger M, Kowalsky W, Riedl T and Kahn A 2012 Adv. Mater. 24 5408
[2] Wang C, Irfan I, Liu X and Gao Y 2014 J. Vac. Sci. Technol. B 32 040801
[3] Haber J and Lalik E 1997 Catalysis Today 33 119
[4] Comini E, Yubao L, Brando Y and Sberveglieri G 2005 Chem. Phys. Lett. 407 368
[5] Rahman M B, Keshmini S H, Yu J, Sadek A Z, Al-Mashat L, Moafi A, Latham K, Li Y X, Wlodarski W and Kalantar-zadeh K 2010 Sensors Actuators B 145 13
[6] Giulio M D, Manno D, Micocci G, Serra A and Tepore A 1998 Phys. Status Solidi a 168 249
[7] Yao J N, Hashimoto K and Fujishima A 1992 Nature 355 624
[8] Chernova N A, Roppolo M, Dillion A C and Whittingham M S 2009 J. Mater. Chem. 19 2526
[9] Geshewa K, Szekeres A and Ivanova T 2003 Sol. Energy Mater. Sol. Cells 76 583
[10] Okumura J, Koerfer F, Salinger C and Wuttig M 2004 J. Appl. Phys. 95 7632
[11] Yao D D, Ou J Z, Latham K, Zhuiykov S, O’Mullane A P and Kalantar-zadeh K 2012 Cryst. Growth Des. 12 1865
[12] Besenov A A, Kirikova M N, Petukhov D I, Allen M, Ryhänien T and Bailey M J A 2014 Nat. Mater. 14 199
[13] Gwinner M C, Pietro R D, Vaynzof Y, Greenberg K J, Ho P K H, Friend R H and Sirringhaus H 2011 Adv. Funct. Mater. 21 1432
[14] Cauduro A L F, dos Reis R, Chen G, Schmid A K, Méthivier C, Rubahn H G, Bossard-Giannesini L, Cruguel H, Witkowski N and Madsen M 2017 ACS Appl. Mater. Interfaces 9 7717
[15] Girotto C, Voroshazi E, Cheyns D, Heremans P and Rand B P 2011 ACS Appl. Mater. Interfaces 3 1244
[16] Bullock J, Cuevas A, Allen T and Battaglia C 2014 Appl. Phys. Lett. 105 232109
[17] Battaglia C et al 2014 Nano Lett. 14 967
[18] Geissbühler J et al 2015 Adv. Phys. Lett. 107 081601
[19] Riley I A, Lee S H, Gedvillas L and Dilllon A C 2010 J. Power Sources 195 588
[20] Chen W, Zhang H, Wang Y, Ma Z and Li Z 2014 Electrochim. Acta 144 369
[21] Zhou J, Song J, Li H, Feng X, Huang Z, Chen S, Ma Y, Wang L and Yan X 2015 New J. Chem. 39 8780
[22] McCarron E M III 1986 J. Chem. Soc., Chem. Commun. 4 336
[23] Julien C, Khelfa A, Hussain O M and Nazri G A 1995 J. Cryst. Growth 156 235
[24] Itoh M, Hayakawa K and Oishi S 2001 J. Phys.: Condens. Matter 13 6853
[25] Kalantar-zadeh K, Tang J, Wang M, Wang K L, Shailosv A, Galatsis K, Koijima R, Strong V, Lech W W A and Kanerde R B 2010 Nanoscale 2 429
[26] Balendhran S et al 2013 Adv. Mater. 25 109
[27] Koike K, Wada R, Yagi S, Harada Y, Sasa S and Yano M 2014 Japan. J. Appl. Phys. 53 05F302
[28] Zou J Y and Schrader G L 1998 Thin Solid Films 324 52
[29] Ohtsuka H and Sakurai Y 2001 Japan. J. Appl. Phys. 40 4680
[30] Ramana C V, Atuchin V V, Kesler V G, Kochubev Y A, Pokrovsky I D, Shuthanandan V, Becker U and Ewing R C 2007 Appl. Surf. Sci. 253 5368
[31] Chang W C, Qi X, Kuo J C, Lee S C, Ng S K and Chen D 2011 CrystEngComm 13 5125
[32] Camacho-López M A, Escober-Alarcón L and Haro-Pontiativeski E 2004 Appl. Phys. A 78 59
[33] Torres J, Alfonso J E and López-Carreno L D 2005 Phys. Status Solidi c 2 3726
[34] Bhosle V, Tiwari A and Narayan J 2005 J. Appl. Phys. 97 083539
[35] Abdellauoui A, Lévêque G, Donnadieu A, Bath A and Bouchikh B 1997 Thin Solid Films 304 39
[36] Hosono K, Matsubara I, Murayama N, Woosuck S and Izu N 2005 Chem. Mater. 17 349
[37] Liu X, Yi S, Wang C, Wang C and Gao Y 2014 J. Appl. Phys. 115 163708
[38] McEvey T M, Stevenson K J, Hupp J T and Dang X 2003 Langmuir 19 4316
[39] Patil P R and Patil P S 2001 Thin Solid Films 382 13
[40] Hall R N, Fenner G E, Kingsley J D, Soltes T J and Carlson R O 1962 Phys. Rev. Lett. 9 366
[41] Khanna V K 2014 Fundamentals of Solid-State Lighting: LEDs, OLEDs, and their Applications in Illumination and Displays (Abingdon: Taylor & Francis)
[42] Balfour J R, Shaw M and Jarosek S 2013 Introduction to Photovoltaics (Burlington, NJ: Jones and Bartlett Learning)
[43] Deb S K and Chopoorian J A 1966 J. Appl. Phys. 37 4818
[44] Ashraf T, Gusenbauer C, Stangl J, Hesser G and Koch R 2015 J. Phys.: Condens. Matter 27 036001
[45] Weber M, Koch R and Rieder K H 1994 Phys. Rev. Lett. 73 1166
[46] Gusenbauer C, Ashraf T, Stangl J, Hesser G, Plach T, Meingast A, Kothleitner G and Koch R 2011 Phys. Rev. B 83 035319
[47] Sarkar A, Wang S, GRAFENEDER W, ARNDT R and KOCHE R 2015 Nanotechnology 26 165203
[48] Koch R 1994 J. Phys.: Condens. Matter 6 9519
[49] Koch R 2010 Surf. Coat. Technol. 204 1973
[50] Chason E, Sheldon B W, Freund L B, Floro J A and Hearne S J 2002 Phys. Rev. Lett. 88 156103
[51] Koch R, Hu D and Das A K 2005 Phys. Rev. Lett. 94 146101
[52] Wang S, Sarkar A, Gruber M and Koch R 2013 J. Appl. Phys. 114 035311
[53] Lee H, LOWE-WEBB R, Yang W and SERCEL P C 1998 Appl. Phys. Lett. 72 812
[54] Mohamed S, Kappertz A, NGRATUIY A, PEDERSEN A T, DRESA R and WUTTIG M 2003 Thin Solid Films 429 135