Temperature-dependent solid-state reactions and the occurrence of the Kirkendall effect are studied in thin film oxide systems applying optical reflection microscopy, X-ray reflectivity, (scanning) transmission electron microscopy, grazing-incidence X-ray diffraction measurements, and SQUID magnetometry. The efficiency of the simultaneous application of different analytical methods for the precise selection and investigation of the most interesting samples is demonstrated first on the example of the Al₂O₃/ZnO system, for which the spinel formation after a solid-state reaction and the formation of Kirkendall voids were already reported. The demonstrated methodology is then applied to study Fe₂O₃/ZnO and CoₓO₃₋₅/ZnO film pairs. The investigations clearly demonstrate the temperature-driven formation of a ferromagnetic spinel by a solid state reaction involving the Kirkendall effect in the Fe₂O₃/ZnO system, already after an annealing at 600 °C for 1 h. We also report on the solid state reaction in the CoₓO₃₋₅/ZnO system after annealing at 700 °C for 1 h, however without the Kirkendall effect and without any evidence of ferromagnetism of the final state.
procedures for samples in which a SSR and a formation of Kirkendall voids can be rapidly identified and then studied in detail.

In the present study we demonstrate an effective way to identify and precisely analyse SSRs and to track the Kirkendall effect in planar thin oxide film systems by combining optical reflection microscopy (ORM), grazing incidence X-ray diffraction (GIXRD), X-Ray reflectivity (XRR), transmission electron microscopy (TEM) and SQUID magnetometry.

We will show that ORM allows fast conclusions on the presence or absence of a SSR in the investigated system already by analysing its light reflection spectrum. A precise phase analysis in the most interesting samples was performed using GIXRD and SQUID magnetometry. It will be shown that the XRR analysis enables the fast selection of those samples in which a formation of Kirkendall voids is suspected. To provide final evidence of the presence of a SSR and the Kirkendall effect in the previously selected samples, TEM, and STEM/EDX analyses were applied.

The proposed analytical procedure was applied to the Al$_2$O$_3$/ZnO system (which is used as a reference) and further to the Fe$_2$O$_3$/ZnO and Co$_3$O$_4$/ZnO thin film systems being the primary objects of the current study.

Sample Preparation and Analysis

The investigated oxide films were deposited using ALD. The ALD process has been implemented on a commercial “Savannah 100” system (Cambridge Nanotech). Commercial Si$_3$N$_4$ (100 nm)/Si (001) and SiO$_2$ (250 nm)/Si (001) wafers were used as substrates. The choice of Si$_3$N$_4$ and SiO$_2$ as buffer materials is justified by their strong thermal stability and inert chemical behavior in the temperature range applied in this study.

For our research a number of different material pairs were prepared in which the following substances were applied: Al$_2$O$_3$, Fe$_2$O$_3$, Co$_3$O$_4$, and ZnO.

Al$_2$O$_3$ and ZnO thin films were deposited at 80 °C using correspondingly the trimethylaluminum (AlMe$_3$, TMA) and diethylzinc (ZnEt$_2$) reaction with water vapor. Both metal-organic precursor sources were maintained at room temperature, whereby the water precursor source was stabilized at 50 °C to obtain a sufficiently high water vapor pressure.

The Fe$_2$O$_3$ and Co$_3$O$_4$ films were deposited by using a chemical reaction between the metalloocene (ferrocene, cobaltocene) and an ozone–oxygen mixture at a chamber temperature of 230 °C. The metalloocene precursor source had a temperature of 100 °C whereby the ozone-gas line was at room temperature. All samples for the study were prepared keeping an excess of the ZnO phase relative to the Al$_2$O$_3$, Fe$_2$O$_3$, and Co$_3$O$_4$ films. In addition, an Al$_2$O$_3$/Fe$_2$O$_3$ film pair was prepared with both films having approximately equal thicknesses.

After the end of the deposition process all samples were divided into pieces, which were respectively annealed at 400, 500, 600, 700, and 800 °C in argon atmosphere for 1 h. The remaining sample pieces were used for the analysis of the as-grown films.

The prepared samples were studied using ORM equipped with a digital camera, GIXRD, and XRR at the E2 banding magnet beam-line of HASYLAB/DESY with incoming photons flux of 10$^8$ mm$^{-2}$ and with an energy of the photons of 11.5 keV. TEM and STEM/EDX analyses were performed in a TEM of type Philips CM20T and a STEM of type Philips CM20FEG, respectively, both working at 200 kV acceleration voltage and both equipped with an energy-dispersive X-ray spectrometer (EDX). SQUID data were collected using a commercial MPMS-XL magnetometer (Quantum Design) in the in-plane sample magnetization setup.

Methodology

Below we provide the analysis of the Al$_2$O$_3$/ZnO system for which the conditions for a SSR involving the Kirkendall effect were previously reported. The sequence of the provided investigation steps is visualized using the flow diagram in Figure 1.

ORM was applied as a preliminary step to identify the presence of a SSR. The argumentation here is the following: Thin oxides possess a high transparency in visible light. The white incoming light is reflected and refracted by each layer and each interface correspondingly. The final reflectance spectrum is then sensitive to both the optical properties of the materials and the interfacial roughness. Below it is shown how both factors contribute to the reflectance spectrum of the sample in which a SSR takes place.

In Figure 2 the ORM images for all as-grown and annealed Al$_2$O$_3$/ZnO samples are compared to those for the Al$_2$O$_3$/Fe$_2$O$_3$ system (and the other systems investigated). It can be seen that for the Al$_2$O$_3$/ZnO system a continuous change of the film color occurs with increasing annealing temperature. The as-grown film shows a gray reflection color whereas the
annealed films change their colors from dark-yellow toward red-violet. For the Al2O3/Fe2O3 system there are no color changes up to a temperature of 700 °C and only small changes of sample color between 700 and 800 °C. The scientific literature supports the fact that the Al2O3/Fe2O3 system exhibits a high chemical resistance against SSRs far beyond 1000 °C.[8] Any SSR between Al2O3 and Fe2O3 can be excluded, due to the maximum annealing temperature of 800 °C of our setup. Under this condition, the slight color changes (from red-orange to red-violet) for this system annealed above 700 °C can be entirely associated with surface and interface roughness changes taking place separately in both films, stimulated by thermally enhanced material diffusion.

On the contrary, for the Al2O3/ZnO system the SSR in the applied temperature range is already known.[2,6,7] It allows us to assume a direct connection between the ORM spectra and the solid-state reaction process in the Al2O3/ZnO system. Furthermore, as an argument for the fact that the substrate material plays a minor role in the temperature-initiated ORM-color changes, we performed additional ORM investigations of annealed Al2O3/ZnO samples grown on Si3N4 substrates. These studies showed that the color palette for the samples grown on Si3N4 – although differing from that of the same films grown on SiO2 substrate (probably due to a different refractive index of silicon nitride) – clearly shows strong temperature-dependent ORM-color variations. We also performed separate studies of single Al2O3 and ZnO films on SiO2 substrates. We found that an Al2O3 film does not reveal any color change within the whole range of investigated temperatures, whereas the ZnO film reveals the same behavior up to 700 °C. Only at 800 °C noticeable color changes were observed in the ZnO film presumably originating from strong recrystallization effects. This allows us to assume that the strong color changes taking place in Al2O3/ZnO multilayer samples after annealing up to 700 °C are mainly driven by a SSR process.

In order to track the formation of Kirkendall pores XRR was applied. The XRR spectra of the as-grown and annealed Al2O3/ZnO samples grown on Si3N4 are presented in Figure 3. It is obvious that for as-grown samples the signals from the Al2O3 and ZnO layers are strongly suppressed. Only the thickness oscillations from the 100 nm thick Si3N4 substrate can be resolved. Relative to the as-grown state, the sample annealed at 400 °C reveals only slight intensity variations without any additional features. At increased annealing temperatures between 500 and 800 °C the corresponding XRR-spectra undergo noticeable changes. To begin with, it is visible that between annealing temperatures of 500 and 700 °C an additional long-period oscillation can be detected at high incidence angles (marked with red arrows in Fig. 3). This oscillation can be associated with a thin layer forming in the multilayer structure. By means of annealing up to 700 °C this oscillation shifts toward lower θ angles. At 800 °C no signal of the corresponding layer structure can be detected. Secondly, by starting at 700 °C, other short-periodic oscillations can be detected at low θ angles. These oscillations become mostly pronounced at 800 °C when the long-periodic signal disappears.

The bright-field cross-section TEM micrographs made on Al2O3/ZnO systems in the as-grown state and after annealing at 600 °C for 1h are shown in Figure 4(a) and 4(b), correspondingly. In the as-grown sample the Al2O3 and ZnO layers can be clearly identified. Both are amorphous and possess pronounced surface roughness. The surface of the amorphous Si3N4 buffer is, on the contrary, noticeably flat. No additional phases can be observed on the Al2O3/ZnO interface. This result correlates well with the XRR-data for the corresponding sample. After annealing at 600 °C strong changes take place within the whole system. Firstly, the roughness of the amorphous Al2O3 layer has been significantly lowered. Secondly, a crystallization of the ZnO layer takes place that reveals a typical contrast pattern with
dominating grain diffraction phenomena. Finally, it is possible to resolve distinct additional contrast variations on the interface between the Al₂O₃ and ZnO films. This interfacial region is shown in Figure 4c with increased magnification. Here, a new dark rough polycrystalline layer sharing its upper interface with the Al₂O₃ film is noticeable. Below this layer a thin bright line can also be distinguished which can be associated with material having much lower density than the surrounding layers. Taking into account that in the Al₂O₃/ZnO system a strong Kirkendall effect occurs between 500 and 700°C, we assume that for the 600°C sample the observed interfacial features correspond to the SSR with a Kirkendall interface between the Al₂O₃ and ZnO films. This interfacial oscillation at 700°C reveals the increased interfacial quality of the spinel film. The disappearance of the oscillations from porous layers at 800°C can be assigned to a re-crystallisation process in the spinel film. At this temperature the voids are removed from the structure by enhanced diffusion processes that had already been shown in previous studies.[6,7]

Results and Discussion

SSR in the Fe₂O₃/ZnO System

In the Fe₂O₃/ZnO system the composition of both contributing oxide layers made from ALD have been securely identified.[2,11] Using GIXRD measurements we found that the as-grown Fe₂O₃ film is already polycrystalline which might initiate a crystallization process in the underlying as-grown amorphous ZnO film. This fact implies that the temperature-driven diffusion processes taking place in the Fe₂O₃/ZnO system might strongly differ from mechanisms previously proposed for the Al₂O₃/ZnO system, where the glass-like (amorphous) nature of the alumina determines the spinel-formation process. Nevertheless, similar to Al₂O₃/ZnO, for Fe₂O₃/ZnO we also expect a temperature-driven SSR, which should end up with the Franklinite spinel phase ZnFe₂O₄.
In Figure 2 the ORM data for a Fe₂O₃/ZnO pair on 250 nm thick SiO₂ buffer demonstrate a temperature-initiated surface color change between 600 and 700°C. It points to a SSR between Fe₂O₃ and ZnO taking place in the mentioned temperature range.

The XRR-spectra for Fe₂O₃/ZnO samples annealed at 600 and 700°C are presented in Figure 6. Similar to the Al₂O₃/ZnO system, here the long-periodic oscillation maximum can be detected for the 600°C-sample which shifts toward lower angles for the 700°C-sample. Taking the Al₂O₃/ZnO system as reference we identify the corresponding signals with a porous layer, which is getting thicker with increasing annealing temperatures. Similar to the Al₂O₃/ZnO system, there are also short-periodic XRR-oscillations visible for the 600°C-samples and disappearing at 700°C – which can be identified as a thick spinel layer becoming rougher at 700°C (probably due to a recrystallization process).

The GIXRD-data for 600- and 700°C-samples shown in Figure 7 also clearly prove the presence of the stoichiometric ZnFe₂O₄ phase without any additional products. The transition from the non-ferromagnetic as-grown Fe₂O₃/ZnO system to the ferromagnetic ZnFe₂O₄ spinel after annealing at high temperatures was also confirmed by the SQUID magnetometry data (see Fig. 7). Interestingly, the data for the in-plane magnetization of the 700°C-sample reveal the specific saturation magnetization of \( \approx 350 \text{emu cm}^{-3} \), which points to the strong ferromagnetic properties of the formed zinc ferrite.

The cross-sectional TEM and STEM data for the Fe₂O₃/ZnO samples annealed at 600 and 700°C for 1 h with corresponding EDX-maps of the constituent materials are shown in Figure 8. Here it is clearly visible that already after 1 h annealing at 600°C the whole Fe₂O₃ film is consumed and a polycrystalline thick “alloy” is formed. According to standard-free (semiquantitative) EDX quantification the Fe:Zn ratio of this “alloy” is close to 2:1 which points to the formation of the stoichiometric ZnFe₂O₄ spinel phase. One can also clearly resolve the nanometer-scale voids entering the remaining thin ZnO film at 600°C, which coalesce to larger voids at 700°C. The recrystallization process taking place in the system at 700°C (see Fig. 6) can also be directly confirmed by the TEM data.

We state that the data from our indirect analyses (ORM, XRR, GIXRD, SQUID) are well consistent with the direct TEM and STEM/EDX observations. This allows us to conclude that in the Fe₂O₃/ZnO system a solid-state reaction accompanied by the Kirkendall effect takes place starting at 600°C.

**SSR in the CoₓO₃/ZnO System**

The final composition of the Co oxide produced using ALD is still a matter of discussions and assumptions in the scientific literature. The situation is complicated because of the fact that in the as-grown state we found our Co oxide films to be amorphous, which makes it impossible to precisely analyze the phase and to identify the oxidation state using X-ray diffraction. Taking into account the fact that the ALD processes that we apply for Co oxide growth employ ozone...
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as an oxidant, we assume that — similar to Fe₂O₃ — the end product of the cobalt oxide film should approach the highest oxidation state of the cobalt ions, i.e. the Co₂O₃ phase. Indeed, the GIXRD study of the CoₓOᵧ system annealed at 700 °C for 1 h revealed the presence of a mixture of Co₂O₃ and CoO phases that offers some possibilities for a SSR in the CoₓOᵧ/ZnO system.

In Figure 2 the temperature-dependent ORM data for the CoₓOᵧ/ZnO system are presented. It is possible to clearly resolve strong color changes pointing to a SSR beginning approximately at 600 °C. In addition, the XRR-data in Figure 9 reveal the morphologically distorted structure for the 600 °C-sample and a formation of a rough thin layer at 700 °C. Similar to the cases described above, this layer might be interpreted as a layer of pores.

A cross-section TEM image of the 700 °C-sample is shown in Figure 10. It reveals the presence of a single substance presumably being a rough polycrystalline mixture of the constituent materials. On the GIXRD spectrum for the corresponding sample shown in Figure 11 we identify three different phases: a CoO phase, a hexagonal (wurtzite) ZnO phase, and a phase close to stoichiometric ZnCo₂O₄. The CoO phase can be clearly identified by two characteristic peaks at 42.6° and 61.4°. In order to confirm our identification of the ZnO and spinel phases, the highly resolved part of the GIXRD spectrum between 29° and 40° is separately presented in Figure 11 for pure ZnO and pure CoₓOᵧ films as well as for the CoₓOᵧ/ZnO sample annealed at 700 °C for 1 h. Here it is possible to see that the peak at 32° on the spectrum from the Co–Zn–O film corresponds to a polycrystalline (100) ZnO reflection. The peak at 36.65° can be identified by comparing the experimental spectrum with tabular data for a bulk ZnCo₂O₄ phase [15] shown in Figure 11.

The experimental peak is close to the strongest reflection of the bulk spinel (36.96°). Furthermore, the spectrum in
Figure 11 for the annealed Co$_x$O$_y$ film reveals two peaks which can be associated with a Co$_2$O$_3$ phase. For the Co–Zn–O film one of these peaks disappears pointing to the transformation of the pure Co$_2$O$_3$ spinel into the Co–Zn–O spinel. The magnetic data in Figure 12 do not reveal any ferromagnetism (FM), neither in the as-grown nor in the annealed samples. In the literature it is assumed that the presence of FM in the ZnCo$_2$O$_4$ spinel is strongly determined by the presence of specific dopants: the n-type and neutral ZnCo$_2$O$_4$ phases are known to be anti-ferromagnetic, whereas the p-type phase shows a ferromagnetic response. This allows us to assume that in our case an n-type doped cobalt-zinc spinel is formed at 700°C.

The STEM/EDX mapping of the 700°C-sample shown in Figure 10 reveals the presence of two distinct phases: the Co-rich grains with correspondingly weaker Zn content and a Zn-rich residual phase with low Co content. According to our GIXRD data we correspondingly associate both phases with a ZnCo$_2$O$_4$ spinel and a remaining ZnO layer mixed with some CoO.

On the contrary to the XRR-data, the TEM observations of the 700°C-sample do not reveal any evidence of voids. On the other hand, the TEM data in Figure 10 reveal a clearly visible thin film at the interface with the SiO$_2$ substrate. EDX studies have shown that the corresponding layer is composed of a Zn–Si–O mixture probably being a result of temperature-driven interdiffusion of Zn atoms into SiO$_2$. So we conclude that for the Co$_x$O$_y$/ZnO system the XRR-data for the 700°C-sample actually reveal the formation of this interdiffusion-related Zn–Si–O layer but not the presence of a porous layer.

By taking all data into consideration we summarize that for the ALD-grown Co$_x$O$_y$/ZnO system the presence of a SSR with the formation of a ZnCo$_2$O$_4$ spinel can be approved. Furthermore, the presence of an additional CoO phase as a
result of high-temperature annealing of Co oxide is assumed to act as an n-type dopant being responsible for the non-ferromagnetic behavior of the cobalt zinc spinel. The SSR in the Co$_{X}O_{Y}$/ZnO system is found to be not accompanied by a Kirkendall effect.

**Conclusions**

In the presented study we have investigated the temperature-dependent solid-state reactions and the Kirkendall effect in thin oxide film pairs grown using ALD. The results of our studies are summarized in Table 1, where the possibilities for the investigated systems to build complex spinel compounds at high temperatures as well as the possibility for the Kirkendall effect are shown. On an example of the ALD-grown Al$_2$O$_3$/ZnO thin film system we demonstrated the effectiveness of employing the large number of analysis methods to securely identify the solid-state reaction as well as to track and to study the Kirkendall effect. Using our methodology we found solid-state reactions in ALD-grown Fe$_2$O$_3$/ZnO and Co$_{X}O_{Y}$/ZnO thin film pairs. For the first time we report on the Kirkendall effect in the Fe$_2$O$_3$/ZnO system during a ZnFe$_2$O$_4$ spinel formation at temperatures between 600 and 700 °C. Furthermore, we report a strong FM in the produced zinc ferrite structure. On the other hand, in the Co$_{X}O_{Y}$/ZnO system the SSR taking place at 700 °C proceeds without any evidence for the Kirkendall effect as well as without any evidence for ferromagnetism.

**Table 1. Summary of the investigated systems.** For each system the presence of a solid-state reaction as well as a Kirkendall effect are separately concluded. Ferromagnetism of the complex spinel after thermal annealing is also shown as a separate property of the investigated systems.

<table>
<thead>
<tr>
<th>System</th>
<th>SSR</th>
<th>Kirkendall</th>
<th>Ferromagnetism of the final spinel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$/ZnO</td>
<td>Yes</td>
<td>Yes</td>
<td>–</td>
</tr>
<tr>
<td>Fe$_2$O$_3$/ZnO</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Co$<em>{X}O</em>{Y}$/ZnO</td>
<td>Yes</td>
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