

Sol–Gel Deposition of Chromium Doped Aluminium Oxide Films (Ruby) for Surface Temperature Sensor Application

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One promising approach for the measurement of surface temperatures is the use of thermographic phosphor coatings. Here the deposition of chromium doped (0–7%) aluminum oxide films (ruby) with respect to this application is investigated. The optical properties of the grown films are presented in a further study. The sol–gel technique is used for film deposition. The method is rather simple and omits an expensive setup, so cheap coatings are easily prepared. Aluminum tri-isopropoxide (ATI) is used as an aluminum source and chromium acetylacetonate ($\text{Cr}(\text{acac})_3$) is used for chromium doping. The deposition process is analyzed by thermogravimetric measurements (TG/DTA). The film morphologies are characterized by scanning electron microscopy (SEM), the chemical compositions are analyzed by energy-dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD) is used for the phase analysis. It is shown that amorphous aluminum oxide is prepared during sol–gel deposition at 563 K. It becomes well ordered ($\alpha\text{-Al}_2\text{O}_3\text{:Cr}^{3+}$) after annealing at 1403 K in an O_2 -atmosphere. The chromium content is homogeneous and identical to the stoichiometry of the aluminum and chromium sources. By using a multicycle deposition procedure well adhering films of around 3 μm thickness are grown.

1. Introduction

The knowledge of surface temperatures is crucial in many scientific or engineering applications. One interesting method to measure surface temperatures is the use of thermographic phosphors. Thereby, the temperature is evaluated from the phosphorescence of the material,^{1,2} which is usually induced by laser light or flash lamp excitation. Several phosphorescence properties are temperature dependent, such as lifetime, intensity, and spectral distribution. They can be used to evaluate the temperature of the films. Often rare-earth-doped ceramics are used as thermographic phosphors,¹ but chromium-doped aluminum oxide (ruby) is also an established material. Its phosphorescence properties are well-understood³ because of its role in the development of lasers and thus ruby was already proposed in the literature as temperature sensor.^{4–9} However, these studies are about bulk materials, e.g., the use of ruby crystals in combination with fiber optics. Less work has been done on ruby films.

It is obvious that thermal phosphor coatings should have a good thermal contact with the substrate underneath, be well

adhering and thermally resistant. Thus, not all coating techniques are useful, e.g., the commonly used method of embedding thermographic phosphors in binders like silicone resin¹⁰ or paint.¹¹ They fail at very high temperatures because of the limited thermal resistance of the binder. Thus, we recently showed the preparation of thin chromium doped ruby films on stainless steel substrates² by chemical vapor deposition (CVD) from organometallic precursors (aluminum acetylacetonate ($\text{Al}(\text{acac})_3$) and chromium acetylacetonate ($\text{Cr}(\text{acac})_3$)). This method omits the use of a binder as the aluminum oxides are in situ grown on the substrates; they are therefore highly thermally resistant. Deposition rates around 3 $\mu\text{m}/\text{h}$ were achieved by CVD and it further turned out in that study that chromium-doped $\alpha\text{-Al}_2\text{O}_3$ is necessary to obtain reproducible phosphorescence.² The metastable γ - and θ -phases and amorphous ruby films are not suited. Deposition temperatures above 1273 K are necessary to grow $\alpha\text{-Al}_2\text{O}_3$, which was achieved by using a cold-wall CVD-setup, low vacuum, and stagnation point flow geometry of the precursor gases.¹² Thus, the CVD method has at least the disadvantage of needing a complex and expensive setup.

In the present study, a simpler deposition method is used for the ruby deposition. The method is based on a sol–gel depositing technique, which was proposed by Bahlawane for the depositing of pure $\alpha\text{-Al}_2\text{O}_3$ as an oxidation-resistant coating of graphite.¹³ In that study aluminum tri-isopro-

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poxyde, diethylene glycol monoethylether, and acetic acid are used to prepare pure aluminum oxide coatings. After annealing the coatings at 1223 K for 10 h, the α -phase is formed. Thus, this receipt seems to be an excellent basis for the preparation of thermographic phosphor (ruby) films: On the one hand, the needed α -phase of aluminum oxide is formed and on the other hand the used chemicals are rather cheap, commercially available and easy to handle. One therefore has the benefit of rather cheap coatings that are obtained with a low-cost setup.

In the literature, it is shown that it is in principle possible to dope sol-gel-deposited aluminum oxide films by partly replacing the aluminum source by an adequate dopant;¹⁴ in that case, aluminum oxide films deposited from inorganic salt were doped with rare-earth elements and the effect on the luminescence was studied. In the present study, the procedure of Bahlawane¹³ for the preparation of pure α -Al₂O₃ films was modified by partly replacing ATI through a chromium source, in order to prepare chromium-doped aluminum oxide (ruby) films. Chromium acetylacetonate was chosen as an adequate chromium source. The crystallization behavior of the doped films is studied and the grown films are structurally and chemically analyzed. For the use of the films as thermographic phosphor coating the phosphorescence properties are important too. The phosphorescence of the sol-gel derived ruby, which is prepared in this study, is shown in a companion paper.¹⁵

2. Experimental Section

Films were deposited by a sol-gel technique basing on the procedure from Bahlawane;¹³ aluminum tri-isopropoxide (ATI), acetic acid (CH₃COOH), and diethylene glycol monoethylether (C₆H₂₄O₃) are used for film preparation. In the present study the procedure is modified by replacing ATI partly through chromium acetylacetonate (Cr(acac)₃) in order to prepare chromium-doped aluminum oxide films. For further details see section 3.

The structure of the prepared films was analyzed by X-ray diffraction using a Bruker X-ray diffractometer (model D8-Advanced) equipped with a copper X-ray tube ($\lambda = 1.5418 \text{ \AA}$) and grazing incidence optics. The angle of incidence was 2° in order to be sensitive to the near surface region. The surface morphology of the films was analyzed with a high-resolution scanning electron microscope (FEI ESEM Quanta 400) working with an acceleration voltage of 10 kV. The SEM was equipped with energy-dispersive X-ray analysis for the detection of the chemical composition of the films. The quantitative chemical analysis was done by the spectrometer software of the carefully calibrated setup. To analyze the crystallization behavior of the sol, we performed thermogravimetric measurements with a "Baehr STA 503"-thermobalance.

3. Results and Discussion

3.1. Sol Preparation. The sol was prepared from aluminum tri-isopropoxide (Sigma Aldrich, 98% pure), chromium acetylacetonate (Merck, 98% pure), acetic acid (KMF, 99.8% pure), and diethylene glycol monoethylether (Fluka, 98% pure) as a solvent. At first, the diethylene glycol monoeth-

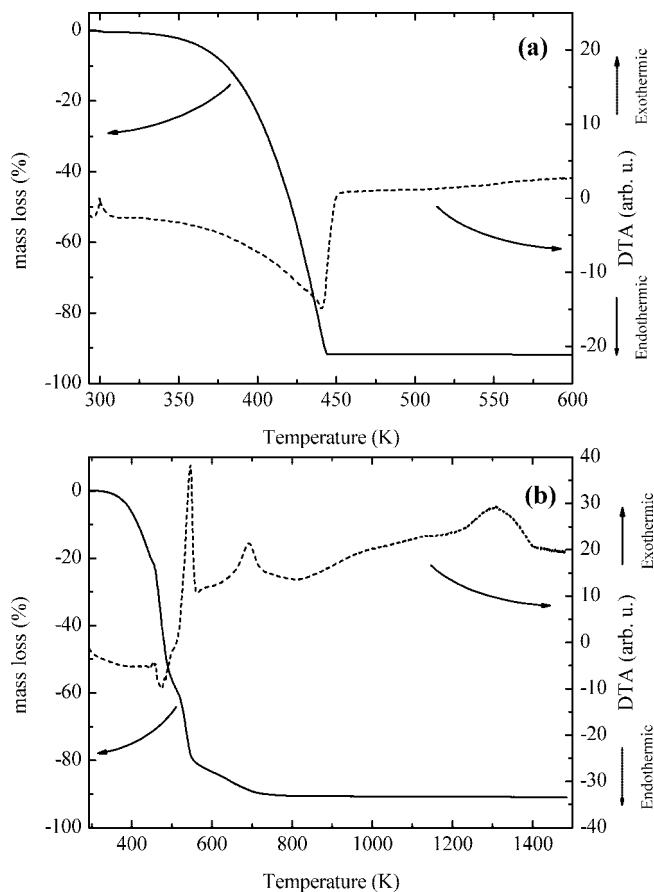


Figure 1. TG and DTA measurements performed during annealing of a sol that was doped with 1.1% Cr. (a) Annealing of the (liquid) sol in a He atmosphere; graph shows the evaporation of the solvent while gel is formed. (b) Annealing of the gel in synthetic air (20% O₂, 80% N₂). Thereby, the analyzed gel was prepared by preannealing the sol at 453 K outside the TG/DTA-setup. Measurement (b) shows the crystallization behavior of the gel.

ylether was heated to 363 K. When the solvent temperature became constant at 363 K, weighed amounts of ATI and Cr(acac)₃ were added while strongly stirring the mixture. After stirring it briskly for 15 min, CH₃COOH was added. Thereby, the molar ratio of the used chemicals [C₆H₂₄O₃:CH₃COOH:ATI:Cr(acac)₃] was [44:3:(1-x):x], where the molar ratio x of the Cr(acac)₃ was varied. In the present study, Cr(acac)₃/ATI-molar-ratios [$x_{\text{Cr(acac)}_3}/x_{\text{ATI}} = y$] between 0 and 0.067 were prepared. It should be mentioned that monitoring of the precise addition of acetic acid is necessary for peptization. After the addition of acetic acid, the temperature was kept constant at 363 K for 5 min while the mixture was stirred slowly in order to obtain a clear sol. It was then slowly cooled to room temperature while being stirred. As a result of this procedure, a clear sol was obtained, which is stable at room temperature for several weeks, meaning that no change in color or viscosity is observed.

3.2. Evaporation and Crystallization Behavior of the Sol. It was observed that the undoped sol becomes a gel after heating in air at temperatures around 453 K.¹³ To check if the addition of chromium acetylacetonate influences the properties of the prepared sol, thermogravimetric measurements (TG/DTA) were performed to study the evaporation behavior (Figure 1a). The doped sol was heated in a helium atmosphere with a heating rate of 5 K/min while the mass

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loss was measured (left ordinate in Figure 1a) and differential thermal analysis (right ordinate in Figure 1a) was performed: The solvent begins to evaporate at 350 K; at 443 K, around 92% of the initial mass is lost. The DTA signal decreases monotonously during the evaporation. Above 443 K, the residual mass of 8% remains constant, indicating that the evaporation of the solvent is completed at ~ 443 K. However, below 443 K, the slopes (TG and DTA) decrease monotonously with increasing temperature, confirming that no other reaction than the evaporation of the solvent takes place, e.g., the pyrolysis of the sol. Thus, there is no indication that the chromium acetylacetonate does influence the gelation process of the sol.

Indeed, gelation is observed after annealing the doped sol in air at 453 K. To study the crystallization behavior of the gel, we performed TG/DTA measurements: The gel, which was prepared outside the thermobalance by annealing the sol at 453 K, was first cooled to room temperature and then heated within the thermobalance to 1500 K while the mass loss (left ordinate in Figure 1b) and the DTA signal (right ordinate in Figure 1b) were measured. The procedure was performed in air, which is similar to the film preparation conditions (see sections 3.3 and 3.4). The heating rate was 10 K/min. At low temperatures (< 730 K), one can observe several exothermic peaks in the DTA signal of Figure 1b while the gel mass is rapidly decreasing with increasing temperature. Two peaks are located at ~ 543 and ~ 690 K; there is probably a third one around 456 K. Thereby the last one is difficult to locate as up to 730 K also endothermic evaporation of the byproduct occurs, which overlaps the DTA signal. Nevertheless, the peaks in the DTA signal and also the mass loss indicate the stepwise decomposition of the gel while presumably forming an aluminum oxide. At temperatures higher than 730 K the residual mass, 10% of the initial gel mass, remains constant; thus one can conclude that the decomposition of the gel is completed at 730 K. Nevertheless, the DTA signal increases slightly above 730 K, and at 1300 K, a broad exothermic peak is observed. This could be originated by the crystallization of the aluminum oxide, probably transforming from an amorphous aluminum oxide into an $\alpha\text{-Al}_2\text{O}_3$, via first forming the γ - and θ -phase of Al_2O_3 (also see section 3.4). It should be mentioned that usually first the γ - and θ -phase of aluminum oxide are formed with increasing temperature when aluminum oxide is grown, e.g., by the oxidation of aluminum,¹⁶ CVD-deposition,^{12,17} or sol-gel deposition.¹³ The phase changes from the metastable γ - and θ -phases to the stable α -phase usually occurs at temperatures around 1273–1373 K.^{12,13,16,17} This is the temperature range at which a peak in the DTA signal (Figure 1b) is observed. Thus, this peak could be originated by the phase transformation of aluminum oxide.

3.3. Material Formation from Drying the Sol. To study the material formed from sol drying, we wetted several silicon substrates with sol at room temperature; they were then placed on a hot heating plate that was preheated to its

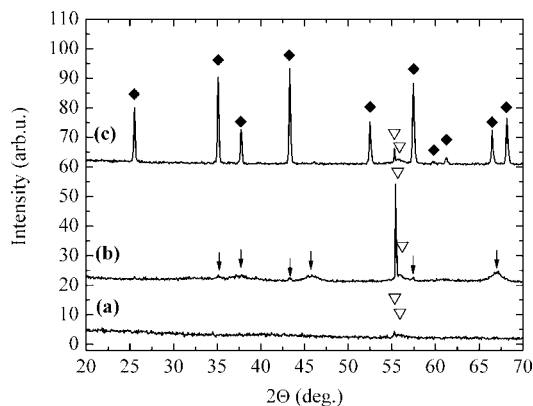


Figure 2. XRD patterns of Cr^{3+} doped aluminium oxide films during anneal treatment. Pattern (a) was measured after film deposition at 563 K. The other patterns were measured after further annealing the film (2 h) in an O_2 atmosphere at (b) 1173 and (c) at 1403 K. The positions of the reflexes of $\alpha\text{-Al}_2\text{O}_3$ (♦) and silicon (▽) are included in the figure. They are taken from refs 19 and 18.

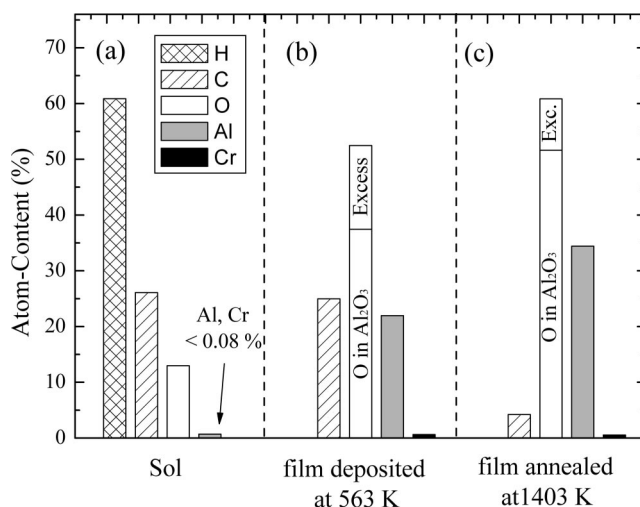


Figure 3. Chemical composition of (a) the sol, (b) the film after deposition at 563 K, and (c) after subsequent annealing the film in oxygen at 1403 K. The composition of the sol (a) was calculated from the weighed amounts of the used chemicals and their molar masses. The film compositions (b, c) were analyzed by EDX. It should be mentioned that hydrogen is not detectable by EDX.

maximum temperature, 563 K, and rapidly being heated in air. After ~ 1 min heating, a yellow coating was formed; nevertheless, the samples were kept for a further 30 s at 563 K in order to finish the reaction completely. They were then removed from the heater and cooled to room temperature. As a result of this procedure, grainy coatings of yellow color were grown on the silicon substrates. It should be mentioned that the same kind of coatings are grown when the deposited sol is first slowly heated at 453 K until a dry and glassy gel is formed, and then being rapidly heated in air at 563 K where the gel decomposition occurs. Obviously, gel formation and decomposition also takes place (but faster) when the deposited sol is rapidly heated to 563 K, because the resulting coatings are the same.

Several of the so-prepared coatings that were deposited from the doped sol (here with $y = x_{\text{Cr}(\text{acac})_3}/x_{\text{Al}} = 0.011$) were further analyzed, namely, by XRD (Figure 2a) with regard to their phase composition, and by EDX (Figure 3b) with regard to their chemical composition. In the XRD

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pattern of such a coating (Figure 2a), only two small reflections are observed, at $2\theta = 55.3$ and 55.8° . They are originated by the silicon substrate (e.g., ref 18). Thus, the coating itself produces no reflections indicating that it is amorphous after deposition at 563 K.

According to EDX analysis (Figure 3b) these coatings consists of around 25 at % carbon, 52.5 at % oxygen, 22 at % aluminum, and traces of chromium ($<0.5\%$). It should be mentioned that hydrogen is not detectable by EDX and that the amount of chromium is not accurately measurable at concentrations below 0.5%, as this is the detection limit of the method. (For a quantitative analysis of the chromium content, see section 3.6.) As comparison, the composition of the initial sol is also shown (Figure 3a); it was calculated from the weighed amount of the used chemicals by using their molar masses. The sol initially consist of 60.8688 at % hydrogen, 26.0878 at % carbon, 12.9574 at % oxygen, 0.0851% aluminum, and 0.0009 at % chromium. Thus when comparing the chemical analysis before (Figure 3a) and after deposition (Figure 3b), one can observe that the relative aluminum content increases with a factor 259 during film deposition, whereas the relative oxygen content increases only by a factor of 4 and the carbon content is decreasing. Therefore, assuming the amount of aluminum remaining constant during film deposition, one can conclude that most of the initial carbon, oxygen, and presumably hydrogen content of the sol is lost during film deposition, either by evaporation of the solvent or by decomposition of the gel. Overall, the amorphous film mainly consists of aluminum oxide. Nevertheless, there is still a large amount of carbon left (25%) after deposition at 563 K, indicating that the decomposition of the gel is not completed at that temperature. This is in good agreement with the TG/DTA measurements of the sol (Figure 1b), showing that the gel is not completely decomposed below 730 K.

3.4. Annealing of the Formed Material. For thermographic phosphor coatings, it is required that the chromium-doped α -phase of Al_2O_3 is grown,² because only this phase shows reproducible phosphorescence. Thus, most of the coatings which were formed from drying the sol at 563 K were subsequently annealed after deposition, in order to reorder the film structure and reduce the carbon contamination. Thereby, the samples were annealed for 2 h at elevated temperatures in a pure oxygen atmosphere at atmospheric pressure. The heating and the cooling rates were 10 K/min. Some of the so-annealed samples were analyzed by XRD (patterns b and c in Figure 2) as a function of the annealing temperature, and some were characterized by EDX (Figure 3c) and SEM (images a and b in Figure 4).

After the film was annealed at 1173 K, the XRD pattern (Figure 2b) was observed. It shows two kinds of reflections: On the one hand, the pattern contains the typical reflections of the silicon substrate (marked with ∇), and on the other hand, several broad reflections are observed (marked with arrows), which originate from the coating itself. These

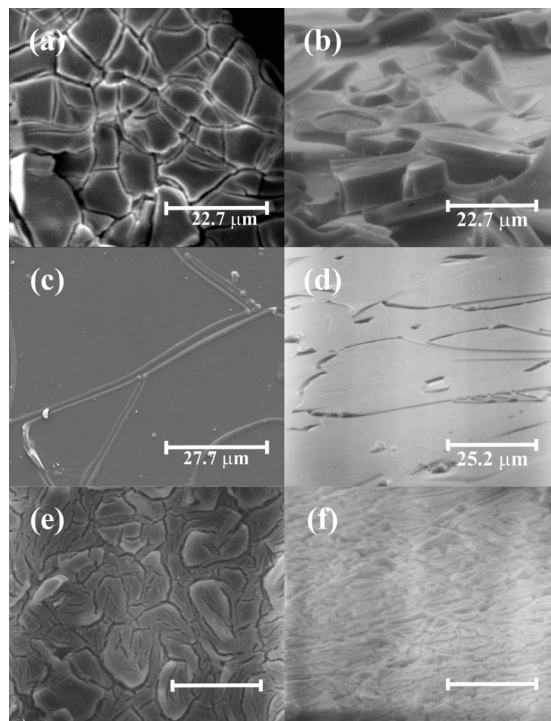


Figure 4. SEM images of sol-gel-deposited aluminium oxide coatings, doped with 1.1% Cr. (a, b) Prepared material after deposition at 563 K and subsequent annealing at 1403 K (2 h) in a pure O_2 atmosphere. (c, d) Coatings after cleaning the samples by sonication. (e, f) $3 \mu\text{m}$ thick ruby coating prepared by repeated sol-gel deposition (for details, see section 3.5). Images (a), (c), and (e) are top views. Images (b), (d), and (f) are taken under 75° to the surface normal.

reflections are very small and very broad; they are actually too small and smeared out for a quantitative analysis of the structure. However, they indicate that crystallization of the coating begins at 1173 K, but the phases are still not distinct after this treatment. After annealing the samples at higher temperatures, their crystallinity increases: After the films are annealed at 1403 K in an O_2 atmosphere, the XRD pattern (Figure 2c) is observed. It clearly shows all the expected reflections of α - Al_2O_3 (marked with \blacklozenge), indicating that a polycrystalline material of the required phase was grown. The reflections are very sharp and thus the crystals are large. Overall, it is shown that crystallization of the material and phase transition to the α -phase occurs at temperatures somewhere between 1173 and 1403 K; at 1403 K, the α -phase is clearly formed. This observation is in good agreement with the gravimetric measurement of the sol (Figure 1b) showing a broad peak at 1300 K, which was probably caused by the ordering of the material.

Some of the chromium-doped samples (here coatings doped with a chromium concentration: $y = x_{\text{Cr(acac)}}/x_{\text{AlTi}} = 0.011$) were subsequently annealed at 1403 K in an O_2 atmosphere and then analyzed by EDX (Figure 3c) and SEM (images a and b in Figure 4). The EDX measurement of such a coating (Figure 3c) reveals the chemical composition: it consists of ~ 60.9 at % oxygen, ~ 34.4 at % aluminum, ~ 0.5 at % chromium, and ~ 4.2 at % carbon. Thus, the material is mainly aluminum oxide, but a carbon contamination (around 3–4% for different samples) is still observable even after the samples are annealed at 1403 K in the oxidizing atmosphere. The aluminum-to-oxygen ratio is around 0.56

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and is thus slightly lower than the expected ratio for Al₂O₃ ($2/3 = 0.67$); obviously, the amount of oxygen is too high for pure Al₂O₃. However, the aluminum oxide is definitively Al₂O₃ according to the XRD analysis. Probably some of the additional oxygen, which is measured by EDX, is partly bonded to the residual carbon atoms. It is further possible that there is also some hydrogen contamination, which is not detectable by EDX. Nevertheless, the chromium doping of the films is confirmed by EDX, and thus the films mainly consist of chromium doped α -Al₂O₃, which is necessary for the application as temperature sensor. It should further be mentioned that the carbon and oxygen contamination, observed by EDX, seem not to influence the phosphorescence properties of the samples, because the phosphorescence spectrum of such a ruby coating and the phosphorescence spectrum of an identically doped synthetic ruby crystal, used for calibration purposes, are identical (see ref 15).

Another indication for the formation of chromium-doped aluminum oxide is the changing of the color during annealing: It changes from yellow into red, which is the typical color of ruby. However, the surface morphology was analyzed by SEM after annealing the samples (images a and b in Figure 4): It shows a grainy film structure with distances between 10 and 100 μm between the grains. This is similar to the surface morphology observed after film deposition at 563 K before the annealing treatment (not shown here).

In principle, one could assume from this cracked film structure that the films might be not well adhering on the silicon substrates. Thus, some annealed ruby coatings were put in an ultrasonic bath filled with distilled water, in order to check the wear properties. It was observed that nearly 60% of the mass of the coating is already lost in the ultrasonic bath after 5 min. However, the remaining 40% stayed constant even after 60 min in the bath. Obviously, they belong to better-adhering parts of the initial coating. SEM images were taken after treating ruby coatings for 40 min in the bath (images c and d in Figure 4). In these images one can observe a rather smooth film. There are still a few cracks observed, but no spallation of the film. Probably the remaining cracks were formed while cooling the samples from 1403 K to room temperature after the annealing process, because the thermal expansion coefficients of alumina and silicon differ strongly. The thicknesses of these smooth films were estimated from the change in mass of the samples during film deposition and the density of α -Al₂O₃ (3.99 g/cm^3) to be $< 1 \mu\text{m}$. The film thickness was also confirmed by several SEM measurements. Obviously, this thin film was covered by the initially observed grains. Several samples were analyzed by XRD; the XRD pattern (not shown here) shows reflexes of α -Al₂O₃, indicating the presence of that phase in the film.

3.5. Improvement of the Wear Properties of Thicker Films. Motivated by the observation of a well-adhering ruby film on the silicon surface, a slightly different deposition procedure was tested in order to produce well-adhering ruby films that are thicker than $1 \mu\text{m}$. Such films may be preferred for the application as thermo sensor, because they show higher phosphorescence intensity than thin films. The deposition procedure bases on the cyclic fabrication of thin

coatings: At the beginning of each deposition cycle, the samples were dipped into the sol and then dried in hot air. Thereby, it is important that the sol film is thin, which is reached by dripping the excess sol before drying the samples. (Thick sol films lead to the formation of cracked ruby films.) After the samples were dried, they were rapidly heated in a Bunsen burner flame for crystallization, resulting in the growth of a thin film. They were then cooled to room temperature, and the deposition cycle was repeated again.

After that procedure was repeated 20 times, the samples were subsequently annealed in an O₂ atmosphere at 1403 K for completing the crystallization of the coating. As result well adhering films were produced with film thickness of around $3 \mu\text{m}$ (estimated from the change in mass of the samples during deposition and the density of α -Al₂O₃). The SEM images of such films are shown in images e and f in Figure 4. The film is cracked, but not spalling. Further, it can not be removed in an ultrasonic bath, indicating that the films are better suited for the application as thermo sensor than the films shown in images a and b in Figure 4. The films were analyzed by XRD. The XRD pattern (not shown here) shows strong reflexes of α -Al₂O₃, indicating the growth of that phase, which is required for the use of these films as temperature sensor.

3.6. Quantitative Analysis of the Chromium Doping.

To study the chromium doping of the aluminum oxide quantitatively, sols with different chromium concentrations y between 0 and 0.067 were prepared. Thereby ($y = x_{\text{Cr}(\text{acac})_3} / x_{\text{ATI}}$) is the ratio of the mole fractions of Cr(acac)₃ and ATI. As both molecules contain only one Cr atom, one Al atom, respectively, y is also the ratio of the chromium and aluminum atoms in the sol. The so-prepared sols were used to deposit chromium-doped aluminum oxide coatings. These films were then analyzed by EDX with respect to their chemical composition.

In all cases the chemical composition of the ruby was similar to the one which is shown in Figure 3c. Only the chromium and aluminum concentrations varied slightly, depending on the chromium concentration y of the used sol. The Cr/Al ratio (of the atoms) in the coatings, which was calculated from the EDX analysis, is plotted in Figure 5 as a function of the Cr/Al ratio y of the used sols, which was calculated from the weighed amounts of Cr(acac)₃ and ATI and their molar masses. Each data point is the average of three single EDX measurements, and the error is the standard deviation. The dashed line shows the slope for equal Cr/Al ratio in the film and the sol.

For Cr/Al ratios y larger than 0.011, one can observe a perfect accordance between the Cr/Al ratios within the ruby and the used sols in Figure 5; they are nearly identically within the range of measurement. For the Cr/Al ratio $y = 0.011$ (sol), a slightly higher ratio was observed in the ruby coatings by EDX. It is believed that this discrepancy is due to the limited resolution of the EDX setup at low chromium concentrations, as the chromium peak in the EDX spectra (not shown here) is very small for such low chromium contents. Nevertheless, for the higher concentrations, it is clearly detectable, and thus the element analysis performed by the software of the calibrated setup is more accurate. One can deduce from Figure 5 that the chromium and aluminum contents within the ruby coatings and the used sols are nearly the same; at least for Cr/Al ratios higher

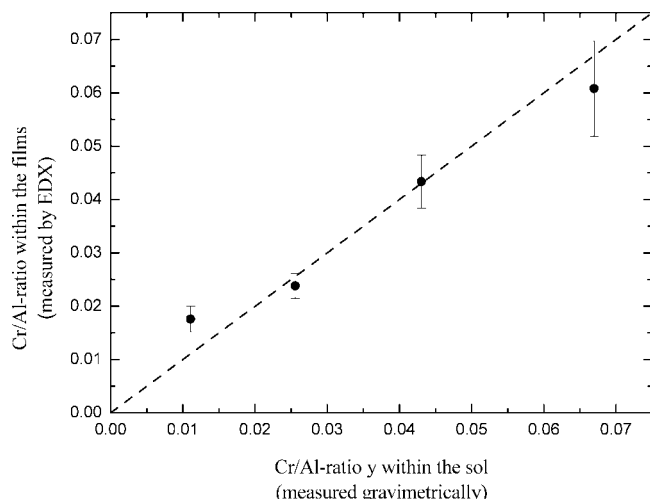


Figure 5. Chromium-to-aluminium (atom) ratio within the prepared film as a function of the chromium-to-aluminium (atom) ratio within the used sol. The chemical composition of the film was analysed by EDX; the one of the sol was calculated from the weighed amounts of the used chemicals and their molar masses. Each data point is the average of three EDX measurements. The error is the standard deviation.

than 0.011 this is doubtlessly proved by EDX. However, there is no plausible reason why the doping should be different at lower Cr concentrations, which are not detectable by EDX. Further, it was observed that the film composition is homogeneous over the whole deposited area. Thus, the sol-gel preparation method is an excellent method for the preparation of precisely doped films, because the doping of the sol is easily controlled gravimetrically.

4. Summary and Conclusion

In summary, we have shown the sol-gel preparation of chromium-doped aluminum oxide films with regard to their

use as thermographic phosphor coating. The sols were prepared from aluminum tri-isopropoxide, diverse solvents, and chromium acetylacetonate. The amount of chromium was varied (chromium-to-aluminum ratios between 0 and 0.067) in order to prepare differently doped films. Ruby was prepared on Si(100) substrates by wetting the substrates with the sols, heating them rapidly up in air to 563 K, and finally annealing them in oxygen at 1403 K. The upper parts of the so prepared coatings are cracked and easily removed, e.g., by cleaning the samples in an ultrasonic bath. Nevertheless, a $<1\ \mu\text{m}$ thick film at the silicon surface is withdrawing such a treatment. Thicker films, around $3\ \mu\text{m}$ thickness, are produced by using a multicycle deposition process.

The chromium content within the ruby was analyzed by EDX. It turned out that the chromium ratio in the ruby is exactly the same as in the sol. However, the doping of the sol is very simple, as it is done gravimetrically. Thus, precisely chromium doped aluminum oxide coatings are easily prepared by this method. Overall, the deposition method has the benefits of being uncomplicated and using commercial available, rather inexpensive compounds; all of which makes it interesting for industrial application.

For the application as thermographic phosphor coating, the phosphorescence properties of the coatings are interesting too. Therefore, ruby was prepared by the above-mentioned procedure and optically analyzed. The results are shown in a companion study.¹⁵

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