Structural transformations and their relation to the optoelectronic properties of chromium oxide thin films

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Abstract. The crystallization behavior of chemically vapor deposited chromium oxide films was characterized by X-Ray diffractometry and the vibrational properties of the films were analyzed by Fourier transform infrared (FTIR) spectroscopy as a function of the annealing temperature and the technological conditions. The effect of the oxygen content in the CVD reactor on the optical characteristics (complex refractive index, optical band gap) was considered.

1. Introduction
Chromium oxide thin films are known as widely applicable in catalysis, solar thermal energy collectors and, as black matrix films, in liquid crystal displays [1, 2]. Other attractive usage of Cr₂O₃ thin films is as electrochromic material, although the chromium oxide system, belonging to the family of transition metal oxides, has been studied only rarely. Many crystalline modifications of Cr oxide exist, such as Cr₂O₃ (corundum), CrO₂ (rutile), Cr₅O₁₂ (three-dimensional framework), Cr₂O₅ and CrO₃ (unconnected strings of CrO₄ tetrahedra). The only stable bulk oxide, Cr₂O₃, is a magnetic dielectric with corundum structure [1]. In the Cr₂O₃ corundum structure, the oxygen atoms form a hexagonal close-packing array. The metal atoms occupy two thirds of the octahedral interstices between two layers. The chromium atoms form graphite-like layers parallel to the oxygen layers. Chromium oxide, Cr₂O₃ consists of the rhombohedral primitive cell, where Cr atoms are eight-coordinated with two oxygen layers. They form CrO₆ distorted octahedra that are linked by faces, edges or corners in such a way that each oxygen atom is linked to four Cr atoms.

In this paper we present results on the structural transformation of chromium oxide films caused by thermal annealing. The films were prepared by low temperature atmospheric pressure chemical vapor deposition (APCVD) and their structure and vibrational properties were studied.

2. Experimental details
Thin Cr oxide films were deposited by way of a low-temperature carbonyl CVD process at atmospheric pressure. The deposition temperature of 200°C was found as optimal leading to deposition of films with good adhesion to the Si, ordinary glass and conductive glass substrates used. The
precursor (Cr(CO)_6) powder was placed in a sublimator and heated up to 70°C. The vapors were carried to the reactor by Ar gas flow and; the reactive gas (oxygen) entered the reactor chamber through a separate line. Since the gas flow ratio of Ar to O_2 is a specific parameter affecting the film structure and composition, it was varied in the range of 1/4, 1/20 and 1/32. The films thickness was about 0.65 μm. After deposition, some of the samples were additionally treated at 500°C in air for one hour.

The crystalline phases in the films were determined with a large-angle (2Θ=0-90°) X-ray Philips X’Pert diffractometer (XRD) working with Cu radiation (λ=0.154056 nm). The Bragg peaks in the XRD spectra were identified using the ASTM database [3]. Assuming a spherical shape of the crystallites, their average grain size was deduced from the Bragg peaks broadening by using the Scherrer’s formula [4]. FTIR spectroscopy was performed in the spectral region of 350-1600 cm\(^{-1}\) by a Shimadzu IRPrestige-21 FTIR Spectrophotometer. The samples studied were deposited on Si substrates and a bare Si wafer was used as background. The spectroscopic ellipsometry (SE) measurements were carried out after each technological step on a Rudolph 436 ellipsometer in the visible spectral range of incident light at an incidence angle of 50°. The optical band gap energy \(E_{\text{og}}\) was derived from the absorption coefficient \(\alpha\) values (\(\alpha=4\pi k/\lambda\)) by constructing \((\alpha h\nu)^{1/2}\) versus photon energy \(h\nu\) Tauc plots. The linear part of the Tauc plot was extrapolated to \(\alpha = 0\); the intersection with the energy axis gave the optical bandgaps \(E_{\text{og}}\) of the films.

3. Results and discussion

All as-deposited films were amorphous, but some nuclei of crystalline phase could be detected in the XRD spectra. Although the XRD data analysis was difficult due to the small amount of film material and the presence of strong Bragg peaks originating from the Si substrate, peaks with very low intensity could be detected within the broad band of the amorphous phase, which corresponded to the strongest peaks of Cr_2O_3 (104) and (111). This is demonstrated in figure 1, where the XRD spectrum of a chromium oxide film deposited at Ar/O_2 gas flow ratio of 1/32 is given.

After annealing at 500 °C, the XRD spectra revealed a fully crystallized film of stoichiometric Cr_2O_3. This is illustrated in figure 2, where the typical XRD spectrum for film deposited at gas flow ratio of Ar/O_2=1/32 is given, and the corresponding crystallographic planes are identified. Although the crystallites are randomly oriented, a certain texture along the (110) crystallographic direction can be seen.

![Figure 1. XRD spectrum of the film deposited at Ar/O_2=1/32. Peaks originating from the Si substrate are denoted by x.](image1)

![Figure 2. XRD spectrum of the film deposited at Ar/O_2=1/32 and annealed at 500°C. The Si peak is denoted by x.](image2)

The lattice parameters obtained, \(a\) and \(c\), of tetragonal Cr_2O_3 were \(a = (4.080 \pm 0.005)\) Å and \(c = (13.003 \pm 0.001)\) Å, which are smaller than those of CVD Cr_2O_3 films grown at Ar/O_2=1/40...
(a = 4.939 Å; c = 13.627 Å) [5] and those cited in [3], namely, a = 4.9587 Å; c = 13.594 Å (JSPDC 38-1479). The crystallites were grown in different crystallographic planes; a larger crystallite average size of 58-61 nm was observed in the preferential (110) crystallographic direction.

The IR spectroscopic analysis was performed on the films deposited at gas flow ratios of 1/4 and 1/20. Figures 3 and 4 present the FTIR spectra of Cr$_2$O$_3$ films before and after annealing. In the spectrum of the as-deposited films, a few absorption bands appear with a tendency to increase the number of bands with decreasing the oxygen content in the deposition ambient. The FTIR bands around 300 and 440 cm$^{-1}$ are assigned to Cr-O bonds, as the IR peak at 401 cm$^{-1}$ is a sign for crystalline Cr$_2$O$_3$ [6]. The latter is in good agreement with the XRD observation (figure 1) and suggests that some crystallites are formed during deposition. The IR bands around 600 cm$^{-1}$ are associated with amorphous Cr$_2$O$_3$ [7]. In figure 3, for the film grown at gas ratio 1/20, a strong, broad absorption band at 540 cm$^{-1}$ and a few superimposed weak bands, namely double peaks around 361 and 372 cm$^{-1}$ and peaks at 385, 403 and 609 cm$^{-1}$ are observed. It must be pointed out that no distinctive bands are detected above 610 cm$^{-1}$. The 545 cm$^{-1}$ band is assigned to the Cr-O bond [6]. For films deposited at 1/4, besides the broad band centered at 519 cm$^{-1}$, a multitude of bands appear - weak bands at 355, 374, 401, 670 and 870 cm$^{-1}$ and well-pronounced bands at 800, 1026 and 1099 cm$^{-1}$. Apparently, these films are substoichiometric and, therefore, chemical bonds of Cr and O atoms in different configurations exist in the oxide network. The IR bands detected at 800 cm$^{-1}$ in the spectrum of the film deposited at Ar/O$_2$=1/4 can be due to Cr-O bonds in CrO$_2$ or CrO$_3$ phases [6]. The well pronounced peaks at 1026 and 1099 cm$^{-1}$ are attributed to the chromyl (Cr=O) vibrations [7].

![Figure 3. FTIR spectra of as-deposited films obtained at Ar/O2=1/4 (1) and 1/20 (2).](image)

![Figure 4. FTIR spectra of films annealed at 500 °C obtained at Ar/O2=1/4 (1) and 1/20 (2).](image)

After annealing at 500°C, the two IR spectra become similar in the 300-700 cm$^{-1}$ region (figure 4). Above that region, the spectrum of the film deposited at Ar/O$_2$=1/20 becomes featureless, while in the IR spectrum of the Cr$_2$O$_3$ film (1/4) strong bands appear at 800 cm$^{-1}$, 1024 and 1096 cm$^{-1}$. In both spectra, the well expressed band at 401 cm$^{-1}$ confirms the crystalline oxide phase, as detected in the XRD pattern (figure 2). In addition, the band at 615.3 cm$^{-1}$ is characteristic for crystalline Cr$_2$O$_3$ [6]. The strong 546 cm$^{-1}$ band, assigned to Cr-O bond [7], points to the films being additionally oxidized to stoichiometric Cr$_2$O$_3$, as proved by the XRD data. The chromyl double Cr=O bonds are still present in the film deposited at 1/4 gas flow, as manifested by the corresponding bands at 1026 and 1099 cm$^{-1}$ [7].

The dispersion spectra for as-deposited and annealed films are summarized in figure 5. The values of the refractive index, $n$, are smaller than those for Cr$_2$O$_3$ [11] suggesting that the films are rather porous. A clear tendency of increasing the $n$ values is observed with increasing the oxygen content during deposition. This can be explained with better oxidation of Cr atoms rather than with film densification, since the IR spectra analysis clearly revealed the substoichiometric oxide structure at lower oxygen contents (figure 3). In the range of 450-820 nm the values of the extinction coefficient, $k$, are close to each other, as is seen in figure 5. The features observed in this region could be
connected with development of defects due to some degree of crystallization taking place in the structure (figure 1). Approaching the absorption edge, the $k$ values increase; the higher the oxygen content, the stronger the absorption. After annealing at 500°C, the values of the refractive index increase (being within 2.2-2.4 in the corresponding spectral range of 820-280 nm) in the whole spectral range studied, thus revealing a better stoichiometric structure. The crystallized films are more transparent, which is reflected in the considerably decreased extinction coefficient values (below 0.3) in the 450-820 nm spectral range.

Using Tauc’s equation, the optical band gap, $E_{\text{og}}$, of the films was estimated with an accuracy of ±0.05 eV. The linear relationship resulted in a better fitting when a direct electron transition model was applied. Similar results have been reported elsewhere [3].

The $E_{\text{og}}$ values are given in the inset in figure 6. For as-deposited films, the $E_{\text{og}}$ values are within 3.18-3.26 eV and tend to increase as the oxygen content in the reactor is increased. These values are characteristic for as-deposited chromium oxide film with an amorphous structure and they are in good agreement with the data reported earlier [11]. After annealing, the optical band gap energy increases to 3.32-3.38 eV, which correlates well with the data reported for CVD Cr$_2$O$_3$ films in crystalline state [11]. The change observed of the $E_{\text{og}}$ values with the Ar/O$_2$ ratio is within the calculation error.

![Figure 5. Spectra of the n and k values for films deposited at gas flow ratios inserted. The empty and full symbols are for films in as-deposited and annealed states, respectively.](image1)

![Figure 6. $(\alpha h\nu)^2$ vs. $h\nu$ dependences for films deposited at gas flow ratio inserted. The empty and full symbols are for films in as-deposited and annealed states, respectively.](image2)

4. Conclusion

The XRD patterns of the CVD chromium oxide films clearly show that during deposition some crystallites are already developed in the amorphous oxide matrix. Annealing at 500°C yields a fully crystallized and stoichiometric Cr$_2$O$_3$ film with crystallites growing larger in the preferential direction. The FTIR analysis supports the XRD results and shows that obviously the oxygen content influences the vibrational properties of CVD prepared chromium oxide films.

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5. References

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