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Optical and microstructural properties of Au alloyed Al–O sputter deposited coatings

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ABSTRACT

This research is focused on the microstructure and optical properties of an Al–O dielectric matrix incorporated with increasing Au contents up to 11 at.%. For the as-deposited coatings, the Au atoms appear to be alloyed into the amorphous oxide matrix, although a small fraction of Au atoms can also be incorporated in the form of very small nanoparticles (<1–2 nm). Precipitation of Au nanoparticles was found in the coatings after annealing at increasing temperatures. Au clustering in the dielectric matrix was able to promote the surface plasmon resonance (SPR) effect, a desirable effect for applications in decorative and sensors fields.

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1. Introduction

Thin films containing metal nanoparticles are of interest to the electronics, glass, chemical sensing/detectors, biotechnology, catalysis, semiconductor and computing industries, due to some specific and extra properties they can confer to the supporting matrix. The main purpose in this area is to promote the formation and distribution of nanoparticles with a specific size and shape either at/near the surface or embedded within a host matrix or a combination of both [1,2]. Most of these applications rely on the localized surface plasmon resonance (LSPR) effect exhibited by the metal nanoparticles, which is governed by the type of metals, the morphology of the nanoparticles and the dielectric properties of the host medium [3,4]. From the available metals, usually Ag and Au are used since other metals like Ti, Cr, Cu, Al and In are either too reactive, or too susceptible to oxidation [5]. The nanometer-sized noble metallic particles give rise not only to the change in color but also to optical enhancements in absorption, Raman scattering and luminescence effects [6].

Among the possible dielectric matrixes, Al-based compounds (Al₂O₃ and AlN) are attractive due to their unique properties. Al₂O₃ in particular has excellent chemical resistance, good mechanical strength, high hardness, good transparency, high abrasive and corrosion resistance, as well as high insulating strength [3,7]. Aluminum oxides are good sensing materials for humidity at near room temperature and show

good stability [8]. At higher temperatures of the order of 450 °C these oxides can also sense H₂, CO₂ and O₂ [9]. Different methods have been used for depositing Au–Al₂O₃ thin films for optical applications, such as radio frequency magnetron co-sputtering from two targets (Au and Al₂O₃) [2,10,11], magnetron co-sputtering from an Al₂O₃ target incrustated with Au pellets [12,13], sol–gel methods [2,14] and Au ion implantation into Al₂O₃ [15].

Several studies concerning the usage of Au/metal oxide nanocomposites for application in areas such as LSPR sensing, catalysis and improved electrochromism have been published for different systems including: Au–TiO₂ [3,16,17], Au–WO₃ [18,19], Au–NiO [20,21], Au–ZnO [20,22], Au–CuO [21,23], Au–Al₂O₃ [2,10–15], Au–Co₃O₄ [21], Au–CeO₂ [17], Au–SiO₂ [24], Au–SnO₂ [25], Au–Fe₂O₃ [26], Au–ZrO₂ [27], Au–MgO [28], Au–V₂O₅ [29], Au–Nb₂O₅ [29], Au–Ta₂O₅ [29], Au–(Y₂O₃)_x(ZrO₂)_{1–x} [17,30,31], Au–MgAl₂O₄ [32], Au–TiO₂–WO₃ [33], Au–TiO₂–NiO [34], Au–TiO₂–NiTiO₃ [35], Au–In_xO_yN_z [36] and Au–SrTiO₃ [37].

In the present study, Al–O thin films were alloyed with gold by reactive co-sputtering method, by means of incrustating different number of Au pieces into an aluminum target and using oxygen as a reactive gas. The films were then thermally annealed for one hour in a protective atmosphere at two different temperatures, 300 °C and 500 °C, in order to promote the segregation of Au nanoparticles in the matrix [4,13,38,39,40]. We have made previous studies on this Al–O + Au system, one regarding the integration/interaction between Au and the Al–O matrix studied through X-ray Photoelectron Spectroscopy (XPS) [41] and another one more focused on the sputtering conditions including

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structure, chemical composition and mechanical properties of such coatings [13]. This paper will be more focused on the structural, microstructural and optical properties of these nanocomposite coatings. Moreover, higher Au contents are adopted in the material system for enhanced surface plasmon effects.

2. Experimental details

The coatings were deposited by pulsed d.c. reactive magnetron sputtering from an aluminum target (15 cm × 15 cm, 99.999% purity), incrustated with different amounts of gold strips (99.999% purity), in a reactive atmosphere (Ar + O₂). Briefly, the strategy consisted of milling rectangular grooves in the target, on each side of the erosion track, and inserting gold strips of varying length and number inside the grooves (each piece having roughly ~1 mm × 10 mm of surface area). The samples were placed in front of the target at a distance of 60 mm. The power density applied to the target was constant at 4 W cm⁻². The deposition pressure was set to 0.55 Pa and the deposition time was 180 min. Before deposition, an ultimate vacuum pressure better than 1 × 10⁻³ Pa was reached. All the coatings were deposited on a silicon (111) wafer. The substrate surface was ion cleaned with an ion gun. The cleaning procedure included first an electron heating step and afterwards an Ar⁺ bombardment step, each for 10 min. A more thorough explanation of the experimental details and procedure can be found in [13].

After deposition, all the thin films were annealed in a horizontal furnace with protective atmosphere (95% Ar + 5% H₂) at a constant pressure of 4 Pa. A heating rate of 30 °C/min and an isothermal period of 60 min were used, after which the furnace was turned off and the samples were left inside until cooled down to room temperature.

The thickness of the films was determined by profilometry using a Perthometer S4P model with a mechanical head of type T1 RFHTB50. The coatings presented thicknesses between 1 and 2 μm. The chemical composition of the coatings was determined by a Cameca SX-50 electron probe microanalysis (EPMA) apparatus with wavelength-dispersive X-ray spectroscopy (WDX) operating at 10 keV. The structure of the films was analyzed by X-ray diffraction (XRD) using a Philips (PANalytical) diffractometer with Co-K_α radiation in grazing incident configuration (GIXRD), with an incident angle of 2°. The XRD parameters, such as the peak position, peak intensity and full width at half maximum (FWHM) were evaluated after fitting the XRD patterns using a Voigt function. The identification of the diffracted phases in the XRD patterns was done by comparing the position of the peaks with those of standard phases listed in the International Centre for Diffraction Data (ICDD) database [42]. The optical properties (transmittance spectra) of the coatings were studied using a UV–Vis–NIR spectrophotometer UV 3101 PC from Shimadzu, equipped with a slit of 1 mm. In some samples, transmission electron microscopy (TEM) was employed, using a JEOL 2010-FEG operating at 200 kV. The TEM specimens were prepared using standard techniques involving cutting disks with a diameter of 3.0 mm, mechanical grinding to 80 μm, dimple grinding in the middle of the disks to 15–20 μm (in a Gatan 656 dimple-grinder) and, finally, ion milling (Ar⁺ bombardment) set at 3 keV energy and 3° incidence angle in a Gatan Precision Ion Polishing System (Model 691).

3. Results and discussion

3.1. Chemical composition

The chemical composition of the Al–O + Au coatings is presented in Table 1. Gold contents up to 11 at.% are achieved. All the coating samples are substoichiometric in aluminum content regarding Al₂O₃, being the aluminum proportionally decreased with increasing gold content. Since the amount of oxygen is kept approximately constant, irrespectively of the Au content, this points to a probable atomic

Table 1

Chemical composition, Au volume fraction (f_{Au}) and elemental Al/O ratio of the Al–O + Au thin films.

Ref.	Atomic % ^a			f_{Au} (%)	Al/O
	Au	Al	O		
AlOAl–0	0	36.2	63.8	0	0.57
AlOAl–5	4.6	32.9	62.6	8.2	0.52
AlOAl–8	7.4	29.1	63.6	12.6	0.46
AlOAl–11	11.3	27.3	61.3	19.1	0.44

^a Standard deviation = ±0.1 at.%.

substitution of Al by Au atoms in the Al–O matrix, in good accordance with what was observed before, in previous studies of the same system [13,41]. Oxidation of Au supported on Al₂O₃ was demonstrated by Pestryakov et al. [43]. Recent studies on the Au–O interaction using density-of-state diagrams and Mulliken charges [44,45] show features from both covalent and ionic bonding types. Au was also found to be atomically integrated in other matrixes, e.g. in Au–yttria-stabilized zirconia (YSZ) nanocomposite films [30].

3.2. Structure

The X-ray diffractograms of the Al–O + Au samples containing different Au contents and annealed at different temperatures are shown in Fig. 1. Irrespective of the Au content and the annealing temperatures, all the Al–O + Au coatings were XRD amorphous regarding any alumina phase. Sputtered alumina coatings are reported to be amorphous for substrate temperatures inferior to 300 °C [46]. Although the number of reported metastable alumina phases exceeds ten, the phase transformations occurs only at high temperatures, around 700–800 °C [47,48].

Regarding the crystallinity of the noble metal in nanocomposite systems, although Au–Al₂O₃ coatings deposited at room temperature were reported to present Au diffraction peaks [11,14], none of the as-deposited and 300 °C annealed samples revealed the presence of gold

Fig. 1. XRD spectra of the Al–O + Au nanocomposites with increasing temperature, for the different Au contents. On the top, the ICDD pattern 04–0784 of the face-centered cubic Au phase is overlapped to facilitate interpretation of results.

Fig. 2. (a) TEM cross-sectional bright-field image of the Al-O + Au film containing 11% at. Au before any annealing. HR-TEM plain view bright-field image and microstructure simulation of the same sample: (b1) and (b2) before annealing; (c1) and (c2) after thermal annealing at 300 °C; (d1) and (d2) after thermal annealing at 500 °C. (e) Histogram and statistical analysis of the nanoparticle separation distances calculated for the (d2) case.

Fig. 2 (continued).

peaks in the X-ray diffractograms. Considering the high amounts of Au present in the coatings, one could expect, at this temperature, Au precipitation in the matrix in the form of Au nanoparticles, due to the increased diffusivity of the metal [11,14,49]. Nevertheless, the absence of gold peaks in the X-ray diffractograms cannot disprove the highly probable precipitation of Au since the presence of small nanoparticles (<2 nm) with low symmetry, not detectable by XRD, can in fact exist. In some experimental and theoretical studies, where the low energy structures of Au nanoparticles were predicted, Au nanoparticles with diameters of 1–2 nm were found to be XRD amorphous [50,51]. In a previous work [13] studying similar alumina coatings doped with Au contents up to 9 at.% we have detected Au precipitation by XRD only after annealing at 400 °C and only in the samples containing more than 7 at.% Au.

Clear signs of Au crystallization were finally detected for all the Au-doped coatings after annealing at 500 °C. By annealing at this temperature, the narrowing of the diffraction peaks suggests coarsening of Au nanoparticles in the nanocomposite coating with increasing Au content, which gives a good indication of moving in the right direction.

3.3. Microstructure

Fig. 2(a) displays the bright-field cross-sectional TEM image of the sample containing 11 at.% Au before any thermal annealing. The presence of a few Au nanoparticles of 5 nm to 25 nm appearing mostly in

the near surface region of the film is revealed (Fig. 2(a)). These nanoparticles are non-representative of the sample's overall microstructure. This indicates that the majority of Au atoms in the as-deposited samples should be atomically dispersed in the amorphous Al–O oxide matrix and/or in the form of very small Au nanoparticles (<1 nm).

The microstructure evolution of one sample (11 at.% Au) with annealing at different temperatures (as-deposited, 300 °C and 500 °C) was studied with planar view HR-TEM observation (Fig. 2(b1),(c1),(d1)). For each case, in order to estimate the amount of Au which is present in the form of nanoparticles and integrated atomically in the oxide matrix, as well as the nanoparticle size distribution and the average interparticle distance, Wolfram Mathematica 8.0 software was used for simulating 30 nm × 30 nm cells with 5 to 10 nm of thickness of an Au–AlO nanocomposite with similar microstructure to the one observed by TEM. Having taken into consideration both the sample preparation step and the high-resolution mode in use, we consider that the thickness of each TEM specimen should be between 5 and 10 nm – thicker samples would lead to dynamical scattering making the image difficult of being interpreted by HR-TEM [52]. Thus by setting the Au volume fraction according to the experiments (Table 1), various cells, having thicknesses between 5 and 10 nm and containing Au nanoparticles with different sizes and size distribution curves (and consequently different numbers of particles), were simulated in order to obtain the best visual match to the experiments. Simulation results of the annealed samples (Fig. 2(c) and (d)) point to an optimum averaged specimen thickness

Fig. 3. (a) Transmittance and (b) Absorbance spectra of the Au-AlO samples at different annealing temperatures (as-deposited, 300 °C and 500 °C). Inset of Fig. 3 (a) shows a close up of transmittance curves of the as-deposited and 300 °C annealed samples. Inset of Fig. 3 (b) shows a close up of absorbance curves of the 500 °C annealed samples.

of 7 nm – for the used Au volume fraction ($f_{Au} = 0.191$), thicker samples would result in overly increased nanoparticle densities. This proved our estimation of sample thickness to be right. Whenever the simulated nanoparticle densities were much higher than that of the real samples for all the cell thicknesses, an alternate sample microstructure was

considered, in which a fraction of the Au atoms would be incorporated into the oxide matrix in the form of Au_2O_3 , and the other fraction would be in the form of Au nanoparticles. This was the case with the as-deposited sample (Fig. 2(b)).

For the as-deposited sample (Fig. 2(b1)), the presence of some 1–3 nm Au nanoparticles dispersed in the amorphous oxide matrix is observed, mostly near the border of the TEM specimen. Au lattice planes within individual nanoparticles are visible. Simulation results (Fig. 2(b2)) suggest that 50% of the Au atoms in this TEM micrograph should be in the form of ~2 nm sized nanoparticles. The remaining Au atoms should be atomically dispersed in the amorphous oxide matrix. This is supported by previous XPS results [41], in which Au–O bonds were detected along with the Au–Au bonds characteristic of small nanoparticles (<1–2 nm), for the samples having more than 7 at.% Au. Some precipitation might have occurred during TEM specimen preparation, contributing to an increased nanoparticle size. TEM sample preparation included an Ar^+ bombardment step in a Precision Ion Polishing System (PIPS) using 3 keV energy, in particular near the edge of holes where the local temperature can rise largely so inducing precipitation of Au nanoparticles as thermal annealing. We have observed before the breaking of the low energy Au–O bonds and subsequent precipitation of Au nanoparticles during XPS depth profiling using Ar^+ ions with 2.5 keV of energy [41]. Another fact supporting this hypothesis is that the bigger Au nanoparticles are only appearing near the specimen edges, where the ion bombardment was more intense.

With the thermal annealing treatments the precipitation and growth of Au nanoparticles becomes apparent. At 300 °C (Fig. 2(c1)) the average Au nanoparticle size is slightly increased. From the microstructure simulation we estimate that the totality of Au atoms (100%) is under the form of ~3.2 nm nanoparticles (Fig. 2(c2)). The Au–O bonds are known to be thermally unstable and should decompose at this temperature [53]. The observed nanoparticle size is higher than expected from the XRD results (which suggests nanoparticle sizes below 2 nm). Again, the Ar^+ bombardment step used during sample preparation could have been responsible for the increased nanoparticle size. At 500 °C (Fig. 2(d1)) the Au nanoparticle's size increases more markedly. Simulation results suggest that the totality of Au atoms is under the form of ~4.6 nm nanoparticles (Fig. 2(d2)).

3.4. Optical properties

In Fig. 3(a) the UV–Vis transmittance spectra of the thin films are shown for the different annealing temperatures. The corresponding absorbance curves are also shown in Fig. 3(b), calculated with the expression [54]: $A = -\log T$, where A is the absorbance and T the

Table 2

Color at transmittance of the thin films deposited on glass substrates, before and after the different thermal annealing treatments.

Annealing temperature	Au content in the film (at.% Au)		
	5	7	11
As-deposited			
300 °C			
500 °C			

Table 3

Color at transmittance of the sample containing 7 at.% Au deposited with different thicknesses on glass substrates, after the thermal annealing at 500 °C.

Sample	Thickness of the film (nm)		
	100	400	1500
7 at.% Au annealed at 500 °C

transmittance (between 0 and 1). Pictures of these coatings in transmittance mode can be seen in Table 2. The coating containing 7 at.% Au was deposited at lower thicknesses to enhance the final coloration, as seen in Table 3.

From the transmittance/absorbance curves present in Fig. 3 we note the absence of the typical SPR extinction peaks, both in the as-deposited and 300 °C annealed coatings. This is an indication that the Au atoms should be incorporated in the coatings either in the form of very small nanoparticles (<1–2 nm) or dispersed in the amorphous Al–O matrix or both [30,38,55]. Moreover, for the as-deposited samples the transmittance curves denote a pronounced red-shift of the absorption edge with the gold content despite only a small reduction of the transmittance maxima (inset of Fig. 3(a)). This translates into a progressive yellowing/browning of the thin films (Table 2). The presence of atomic Au in the nanocomposites can make their optical properties to deviate significantly from what would be expected for Au nanoparticles alone [30]. The red-shift in the absorption edge is ascribed to a narrowing of the optical band gap, suggesting a strong effect of the gold concentration in the electronic properties of the coatings. Au-related defects could be acting as donors in Al–O such that a large defect density could likely induce a merging of the donor and conduction bands [56]. The evidence of band-gap narrowing can also be found by looking closely at the absorption tails of Au–Al–O samples in the inset of Fig. 3(a). Impurity transitions are known to cause a smearing of the absorption edge compared with the abrupt edge found at the band gap of pure compounds [57]. Overall these results could suggest an increasing metallic character of the coatings with the Au content [56,58].

After thermal annealing at 300 °C, the absorption edge of the sample containing 4.5 at.% Au red-shifts, whereas the absorption edge of the samples containing 7 at.% Au and 11 at.% Au blue-shifts. This blue-shift was responsible for the less intense browning of these two coatings at this temperature, when compared to the as-deposited samples (Table 2). The local precipitation of very small nanoparticles should be enhanced in the samples containing higher Au contents, with a subsequent reduction in the electronic states that were probably formed around the band edges of the Al–O compound. For the sample containing less Au content the Au atoms are more distant from each other, making more difficult its precipitation at this relatively low temperature.

After annealing at 500 °C, SPR peaks are finally observed in the transmittance/absorption spectra (Fig. 3). This is especially evidenced in the two samples containing higher Au contents. The SPR absorption peaks appear close to $\lambda = 550$ nm, the expected SPR peak position for the case of Au nanoparticles embedded in a low refractive index medium like alumina ($n \approx 1.6$) [11,12]. The absorption of light in this wavelength region was responsible for the appearance of different purple-violet–magenta tones in the thin films (Table 2). The effect of sample thickness on the final color of the thin films is depicted in Table 3, for the sample containing 7 at.% Au. For the sample with the highest Au content (11 at.% Au) the SPR peak appears asymmetrically broaden (with a prolonged tail in the higher wavelength region, as seen in the inset of Fig. 3(b)), suggesting several contributions in this absorbance region. There is also a generalized loss of transmittance throughout the visible spectrum, especially in the higher wavelength region. This loss in transmittance is responsible for the darker color tones of this

sample (Table 2). From the Mathematica simulation (Fig. 2(d2)) a mean interparticle distance (center-to-center) of $D \approx 11.3$ nm was determined, resulting in a mean separation distance (surface-to-surface) of $d \approx 6.7$ nm ($d = D - 2R$). Although on average the separation distances are greater than the diameter of the nanoparticles ($2R \approx 4.6$ nm), from the statistical analysis (Fig. 2(e)), we estimate that for such a microstructure case roughly 30% of the nanoparticles have separation distances that are lower than the average nanoparticle size. This means that roughly 30% of the nanoparticle's population should be affected in a greater or lesser degree by interparticle effects, which are responsible for a red-shift and a broadening of the SPR peak [3,55,59]. This explains the asymmetric shape of the perceived SPR peak, with different contributions appearing overlapped. We speculate that the overall loss in transmittance is due to the presence in the thin film of a great density of small point defects related to oxygen release, after the breaking of the fragile Au–O bonds [13], generating scattering effects.

4. Conclusions

Al–O based dielectric matrix coatings were co-deposited with different Au contents, up to 11 at.% Au. A progressive decrease of the Al element with increasing Au content was observed (for an approximately constant O content). From the X-ray diffraction results, the absence of Au diffraction peaks was observed for the as-deposited and 300 °C annealed samples, suggesting that the Au atoms could be either dispersed in the amorphous matrix atomically and/or in the form of very small nanoparticles (<1–2 nm). TEM analysis confirmed that the Au atoms were both atomically dispersed in the amorphous oxide matrix and in the form of very small nanoparticles. However, the observed Au nanoparticles in the as-deposited samples were likely to have precipitated during the preparation of TEM specimen.

Optical analysis was in good accordance with the previous results, showing no signs of SPR absorption for the as-grown and 300 °C annealed samples. Moreover, a strong influence of the Au content in the electronic properties of the films was detected, with a progressive decrease in the optical band gap with the Au content. As a result, these coatings showed increasingly intense yellow-brown color tones with the Au content. After annealing at 500 °C SPR absorption peaks were finally perceptible, attributed to the presence of larger Au nanoparticles in the films (>2 nm), as characterized by HR-TEM and XRD. By annealing at this temperature the coatings showed different tones of purple-violet–magenta colors.

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References

- [1] G. Walters, I.P. Parkin, *J. Mater. Chem.* 19 (2009) 574–590.
- [2] G. De, S. Bhattacharyya, *J. Mater. Chem.* 18 (2008) 2816–2824.
- [3] N.M. Figueiredo, T. Kubart, J.A. Sanchez-García, R. Escobar Galindo, A. Climent-Font, A. Cavaleiro, *J. Appl. Phys.* 115 (2014) 063512.
- [4] M. Torrell, R. Kabir, L. Cunha, M.I. Vasilevskiy, F. Vaz, A. Cavaleiro, E. Alves, N.P. Barradas, *J. Appl. Phys.* 109 (2011) 074310.
- [5] H. Deng, D. Yang, B. Chen, C.-W. Lin, *Sensors Actuators B* 134 (2008) 502–509.
- [6] Y. Hosoya, T. Suga, T. Yanagawa, Y. Kurokawa, *J. Appl. Phys.* 81 (1997) 1475–1480.
- [7] Y. Li, S. Zhang, Y. Liu, T.P. Chen, T. Sriharan, C. Xu, *J. Nanosci. Nanotechnol.* 9 (2009) 4116–4120.
- [8] G. Eranna, B.C. Joshi, D.P. Runthala, R.P. Gupta, *Crit. Rev. Solid State Mater. Sci.* 29 (2004) 111–188.
- [9] T. Seiyama, S. Kagawa, *Anal. Chem.* 38 (1966) 1069–1073.
- [10] S. Cho, S. Lee, S.-g. Oh, S.J. Park, W.M. Kim, B.-k. C, M. Chung, K.B. Song, T.S. Lee, S.G. Kim, *Thin Solid Films* 377–378 (2000) 97–102.
- [11] J. Wang, W.M. Lau, Q. Li, *J. Appl. Phys.* 97 (2005) 114303.
- [12] S. Hazra, A. Gibaud, C. Sella, *Appl. Phys. Lett.* 85 (2004) 395–397.
- [13] N.M. Figueiredo, C. Louro, R.E. Galindo, A. Climent-Font, A. Cavaleiro, *Surf. Coat. Tec.* 206 (2012) 2740–2745.
- [14] T. Ishizaka, S. Muto, Y. Kurokawa, *Opt. Commun.* 190 (2001) 385–389.
- [15] Y. Takeda, O.A. Plaksin, H. Wang, K. Kono, N. Umeda, N. Kishimoto, *Opt. Rev.* 13 (2006) 231–234.
- [16] P.R. Ohodnicki, C. Wang, S. Natesakhawat, J.P. Baltrus, T.D. Brown, *J. Appl. Phys.* 111 (2012) 064320.
- [17] N.A. Joy, P.H. Rogers, M.I. Nandasiri, S. Thevuthasan, M.A. Carpenter, *Anal. Chem.* 84 (2012) 10437–10444.
- [18] M.Z. Ahmad, A.Z. Sadek, M.H. Yaacob, D.P. Anderson, G. Matthews, V.B. Golovko, W. Wlodarski, *Sensors Actuators B* 179 (2013) 125–130.
- [19] N.M. Figueiredo, Y.T. Pei, J.T.M. De Hosson, A. Cavaleiro, *Surf. Coat. Technol.* 280 (2015) 201–207.
- [20] E.D. Gaspera, M. Guglielmi, A. Martucci, L. Giancaterini, C. Cantalini, *Sensors Actuators B* 164 (2012) 54–63.
- [21] M. Ando, T. Kobayashi, M. Haruta, *Catal. Today* 36 (1997) 135–141.
- [22] J. Manna, T.P. Vinod, K. Flomin, R. Jelinek, *J. Colloid Interface Sci.* 460 (2015) 113–118.
- [23] M. Ando, T. Kobayashi, S. Iijima, M. Haruta, *Sensors Actuators B* 96 (2003) 589–595.
- [24] P.R. Ohodnicki, M.P. Buric, T.D. Brown, C. Matrangola, C. Wang, J. Baltrus, M. Andio, *Nanoscale* 5 (2013) 9030–9039.
- [25] A. Katoch, J.-H. Byun, S.-W. Choi, S.S. Kim, *Sensors Actuators B* 202 (2014) 38–45.
- [26] C.-H. Tseng, T.C.K. Yang, H.-E. Wu, H.-C. Chiang, *J. Hazard. Mater.* 166 (2009) 686–694.
- [27] X. Zhang, H. Shi, B.-Q. Xu, *J. Catal.* 279 (2011) 75–87.
- [28] S.A. Fuente, R.M. Ferullo, N.F. Domancich, N.J. Castellani, *Surf. Sci.* 605 (2011) 81–88.
- [29] I. Sobczak, K. Jagodzinska, M. Ziolek, *Catal. Today* 158 (2010) 121–129.
- [30] G. Sirinakis, R. Siddique, K.A. Dunn, H. Efstathiadis, M.A. Carpenter, A.E. Kaloyeros, *J. Mater. Res.* 20 (2005) 3320–3328.
- [31] N.A. Joy, C.M. Settens, R.J. Matyi, M.A. Carpenter, *J. Phys. Chem. C* 115 (2011) 6283–6289.
- [32] A. Villa, A. Gaiassi, I. Rossetti, C.L. Bianchi, K. van Benthem, G.M. Veith, L. Prati, *J. Catal.* 275 (2010) 108–116.
- [33] M. Rusu, M. Baia, Z. Pap, V. Danciu, L. Baia, *J. Mol. Struct.* 1073 (2014) 150–156.
- [34] E.D. Gaspera, M. Guglielmi, S. Agnoli, G. Granozzi, M.L. Post, V. Bello, G. Mattei, A. Martucci, *Chem. Mater.* 22 (2010) 3407–3417.
- [35] E.D. Gaspera, M. Pujatti, M. Guglielmi, M.L. Post, A. Martucci, *Mat. Sci. Eng. B* 176 (2011) 716–722.
- [36] H. Steffes, A. Schleunitz, U. Gernert, R. Chabichovsky, E. Obermeier, *Microelectron. Eng.* 83 (2006) 1197–1200.
- [37] S. Christke, C. Katzer, V. Grosse, F. Schmidl, G. Schmidl, W. Fritzsche, J. Petschulat, T. Pertsch, M. Rettenmayr, *Opt. Mater. Express* 1 (2011) 890–897.
- [38] N.M. Figueiredo, F. Vaz, L. Cunha, S.E. Rodil, A. Cavaleiro, *Surf. Coat. Technol.* 255 (2014) 130–139.
- [39] M. Torrell, P. Machado, L. Cunha, N.M. Figueiredo, J.C. Oliveira, C. Louro, F. Vaz, *Surf. Coat. Technol.* 204 (2010) 1569–1575.
- [40] A. Sivasankar Reddy, N.M. Figueiredo, A. Cavaleiro, *Vacuum* 86 (2011) 1323–1327.
- [41] N.M. Figueiredo, N.J.M. Carvalho, A. Cavaleiro, *Appl. Surf. Sci.* 257 (2011) 5793–5798.
- [42] <http://www.icdd.com/>
- [43] A.N. Pestryakov, V.V. Lunin, A.N. Kharlanov, D.I. Kochubey, N. Bogdanchikova, A.Y. Stakheev, *J. Mol. Struct.* 642 (2002) 129–136.
- [44] Z.-P. Liu, P. Hu, *J. Am. Chem. Soc.* 124 (2002) 14770.
- [45] F. Tielens, L. Gracia, V. Polo, J. Andrés, *J. Phys. Chem. A* 111 (2007) 13255–13263.
- [46] J.M. Schneider, W.D. Sproul, R.W.J. Chia, M.-S. Wong, A. Matthews, *Surf. Coat. Technol.* 96 (1997) 262–266.
- [47] I. Levin, D. Brandon, *J. Am. Ceram. Soc.* 81 (1998) 1995.
- [48] K. Wefers and C. Misra, *Oxides and hydroxides of aluminum*, Alcoa Technical Paper No. 19, revised (Alcoa Laboratories, Pittsburgh, 1987).
- [49] S.H. Cho, S. Lee, D.Y. Ku, T.S. Lee, B. Cheong, W.M. Kim, K.S. Lee, *Thin Solid Films* 447–448 (2004) 68–73.
- [50] A. Sebetci, Z.B. Guvenç, *Model. Simul. Mater. Sci. Eng.* 13 (2005) 683–698.
- [51] T.G. Schaaff, M.N. Shafigullin, J.T. Khoury, I. Vezmar, R.L. Whetten, W.G. Cullen, P.N. First, *J. Phys. Chem. B* 101 (1997) 7885–7891.
- [52] D.B. Williams, C.B. Carter, *Transmission Electron Microscopy – A Textbook for Materials Science*, Springer Science, New York, 2009.
- [53] N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, 2nd ed. Butterworth-Heinemann, 1997.
- [54] O. Stenzel, *The Physics of Thin Film Optical Spectra*, Springer-Verlag, Berlin, Heidelberg, 2005.
- [55] U. Kreibig, M. Vollmer, *Optical Properties of Metal Clusters*, Springer, New York, 1995.
- [56] Y.R. Park, K.J. Kim, *Solid State Commun.* 123 (2002) 147–150.
- [57] M. Fox, *Optical Properties of Solids*, Second edition Oxford University Press, New York, 2010.
- [58] A.P. Roth, J.B. Webb, D.F. Williams, *Phys. Rev. B* 25 (1982) 7836.
- [59] M. Quinten, *Optical Properties of Nanoparticle Systems – Mie and Beyond*, Wiley-VCH, Germany, 2011.