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Violet-blue photoluminescence in aluminium oxide films prepared by ultrasonic spray pyrolysis

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Abstract

Violet-blue photoluminescent emission has been observed in aluminium oxide films deposited by the ultrasonic spray pyrolysis process at atmospheric pressure, using solutions of 0.05 M aluminium acetylacetonate in a mixture of two parts of deionised water and two parts of methanol and aluminium chloride in the same solvent mixture. The films were deposited at substrate temperatures in the range from 240 to 440°C. The refractive index has values lower than those associated with crystalline phases of Al₂O₃. These values are due to the amorphous nature of the deposited films and the incorporation of organic or chlorine related radicals. The photoluminescence excitation spectra show two peaks located at 281 and 371 nm, the latter being with higher intensity. The photoluminescent emission spectra are constituted by a broad band with a peak located at 405 nm and, it has a maximum intensity for the sample prepared at 380°C. It is suggested that this emission is associated with radiative recombination from an excited level of the aluminium ions. The photoluminescence emission spectra can be formed by several contributors, for all the samples, which suggests that these emissions are associated with aluminium ions incorporated in excess in aluminium oxide host on different sites, as it has been observed in several glasses. From an Arrhenius plot of the intensity of the peak located around 405 nm, as a function of substrate temperature an activation energy of 1.16 eV has been calculated. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Luminescent films have several potential applications, one of them is as optical active layer in flat panel displays [1]. A considerable research effort has been made on (1) the film deposition techniques and (2) different types of materials and

(3) suitable dopants. The main goal of these efforts is to obtain good-quality films, emitting in the three basic colors. However, efficient blue emitting material has been difficult to produce and there is an intensive research activity to resolve this problem [2]. Rare earth dopants, cerium, thulium and several of their compounds have been used to produce blue emitting materials [3,4]. In that case the blue emission comes from the transitions of the 5d to the 4f electronic energy states of the Ce³⁺ ion and for the Tm³⁺ ion [5]. Recently, blue

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photoluminescence was reported from CeCl_2 doped aluminium oxide prepared by the spray pyrolysis technique using a pneumatic nozzle [6]. However, in that case it was observed that to obtain the blue emission it was necessary to dope the aluminium oxide host with a luminescent molecular centre formed by the CeCl_2 molecule, which is possible if the films are prepared at relatively low substrate temperature.

The spray pyrolysis technique has two versions, (a) with the fine mist produced by a pneumatic nozzle [7] and (b) that where the fine drops are ultrasonically produced, also called pyrosol process [8]. Both versions are suitable to deposit large area thin films. They are probably the easiest and lowest cost, nonvacuum techniques to prepare thin films. The spray pyrolysis process with pneumatic atomisation has been used for deposition of several kind of materials, like: transparent conductive contact [9], semiconductors [10], luminescent [11], etc. On the other hand, there are several reports which describe the pyrosol process [8,12]. In this process when an ultrasonic beam is directed at a gas–liquid interface, the formation of a geyser takes place. This geyser is accompanied by the generation of a spray, resulting from vibrations at the liquid surface and cavitation at the gas–liquid interface. This spray is carried by a gas and directed onto the heated surface of the substrate where a chemical reaction takes place leaving a solid film. This technique has been used to prepare several materials, like: metals [8], sulfides [13] and oxides [14].

In this work, we report the photoluminescent characteristics at room temperature of undoped aluminium oxide films prepared by the pyrosol process. The light emission spectra of these films show basically a broad band with its peak located at about 405 nm. The relative intensity of the band emission depends on the deposition parameters such as substrate temperature and the composition of the solvent used to prepare the start solution.

2. Experimental

The aluminium oxide films were deposited by pyrosol process. First, the start solution was 0.05 M aluminium acetylacetonate (AlAAc) in a mixture of

two parts of methanol and two parts of deionised water. To obtain a complete dissolution of the AlAAc, 3 ml of acetic acid was added per liter of start solution. It is known that organometallic compounds have suitable thermodynamic and chemical properties to ensure a vapour phase chemical reaction [15]. The substrate temperature during deposition (T_s) was varied between 240 and 440°C, in steps of 20°C. The substrates used in this work were pyrex glass slices and (1 0 0) n-type silicon single crystals. The deposition time was 120 min, in all cases. The thickness of the deposited films was measured by means of a Dectak IIA profilometer. The films thicknesses were in the range from 290 to 630 nm. The refractive index of the films was measured with a Gaertner 117A ellipsometer using the 632 nm line from an He–Ne laser. The crystallinity of the samples was analyzed by X-ray diffraction measurements by means of a Siemens D500 diffractometer, although all the studied films were of amorphous nature. Relative chemical composition analyses were carried out by energy dispersive spectroscopy (EDS) using an Oxford Link Pentafet System. The photoluminescent properties, emission and excitation spectra, were measured with a Fluoromax Spex spectrofluorometer sensitive in the range 200–850 nm. The excitation light was produced with a Xenon lamp. Measurements of the emitted light intensity as a function of the temperature in the range 160–300 K (due to limitations in the equipment) were made. To observe the effect of the composition of the solvent and the effect of changing the aluminium source compound, the composition of the mixture was varied to (i) pure deionised water and (ii) a mixture of three parts of deionised water and one part of methanol. On the other hand, using a mixture of two parts of deionised water and two parts of methanol, the aluminium source material was changed to aluminium chloride instead of AlAAc. In these cases depositions at $T_s = 380^\circ\text{C}$ were made, taking into account the substrate temperature for highest emission intensity observed in the previous case.

3. Results and discussion

Fig. 1 shows the refractive index (n) as a function of the substrate temperature. It can be observed

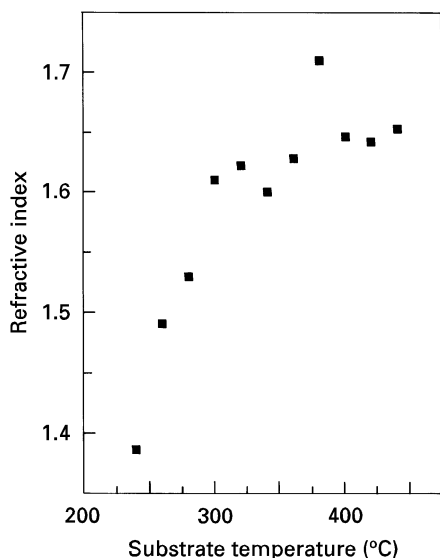


Fig. 1. Refractive index as a function of the substrate temperature from aluminium oxide films deposited by pyrosol.

that for substrate temperatures up to 300°C, the value of n drastically increases, and for higher T_s it acquires an almost constant value. However, for the substrate temperature of 380°C the refractive index has a maximum. The low values of n for low T_s are explained considering that for those T_s , there are some organic radicals incorporated into the deposited films and that these films are of porous nature [16]. A similar effect has been observed in zinc oxide films deposited by spray pyrolysis using a pneumatic nozzle, in that case the source material was zinc chloride [7]. The microprobe analyses of the deposited materials show that the incorporation of chlorine atoms decreases as the substrate temperature increases, this fact is associated with the incomplete decomposition of the zinc chloride molecules, which is thermally assisted. Also, similar results were obtained for low substrate temperature silicon dioxide deposited by plasma enhanced chemical vapour deposition using SiF_4 as silicon source material [17]. There are some deposition conditions in which the chemical decomposition of the SiF_4 molecule is not complete, leaving fluorine radicals incorporated in the films which results in values of the refractive index lower than that of the stoichiometric SiO_2 . For higher substrate temper-

atures the chemical reaction is carried out in such a way that there are less organic radicals incorporated in the deposited material, with a better aluminium oxidation, and with a more dense microstructure, because at those T_s values the organometallic source compound is decomposed and a real chemical vapour deposition process takes place [15]. In general, metal rich oxides have higher values of refractive index than those observed for stoichiometric oxides. In the present case, the unexpectedly high value of n for the sample with $T_s = 380^\circ\text{C}$, is associated with a higher incorporation of non-oxidized aluminium atoms in the deposited film, giving place to an aluminium rich oxide. For the highest T_s used, the decomposition of the organometallic source compound and the subsequent oxidation of the aluminium atoms are almost complete, but due to the growth process of the films they result in amorphous nature as was observed from the X-ray diffraction measurements and then the refractive index takes lower values. The reported refractive index values for α and γ crystalline phases of Al_2O_3 are 1.765 and 1.70, respectively [18]. In general, the n values measured in amorphous materials are lesser than those observed in the crystalline phases with the same chemical composition. It appears that this is the case in the present work. The n values measured in samples prepared at $T_s = 380^\circ\text{C}$, when the solvent composition was changed are in the range from 1.658 to 1.730, indicating both (i) a low incorporation of organometallic radicals and (ii) a better oxidation of the aluminium atoms due to the higher water concentration in the solvent. Meanwhile, when the aluminium source material was changed to aluminium chloride, n had a value of 1.644, which is of the same order of magnitude than those obtained when the aluminium source material was organometallic.

The luminescence excitation spectrum shown in Fig. 2 was obtained for the sample prepared at $T_s = 380^\circ\text{C}$. This spectrum shows two peaks, one located at 281 nm and another, with higher intensity, located at 371 nm. All the samples have similar excitation spectra. These spectra were measured with the emission kept constant at a wavelength of 405 nm. Fig. 3 shows the PL emission spectra, with excitation of 371 nm, for the samples prepared at substrates temperatures of (a) 240°C, (b) 320°C,

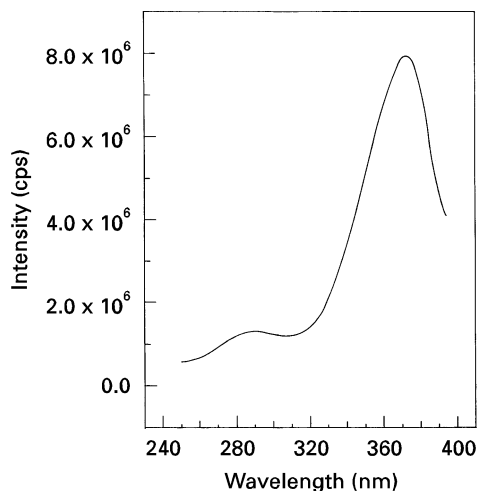


Fig. 2. Excitation spectrum for an Al_2O_3 film deposited at substrate temperature of 380°C . The emission wavelength was kept constant at 405 nm.

(c) 380°C and (d) 440°C , respectively. It should be cleared that these samples have similar thickness ($\cong 450$ nm). It is observed that all the spectra show a broad band emission whose maximum shows a small shift, which depends on the substrate temperature deposition. Fig. 3e shows the PL spectrum of the sample prepared with aluminium chloride as source material. In this case, the incorporation of chlorine atoms in the deposited film instead of organic radicals is expected, since it is known that films deposited at that substrate temperature using chlorides as source materials show, in general, the incorporation of chlorine atoms in a relatively low concentration [7].

Fig. 4 shows the photoluminescence spectra, with an excitation wavelength of 281 nm, for samples prepared at (a) 240°C , (b) 320°C , (c) 340°C and (d) 420°C . In general, the PL emission intensity is lower than that observed in Fig. 3, this fact is associated with the lower emission intensity observed in excitation spectrum of Fig. 2. The spectra in this figure show a similar trend than that observed for excitation with 371 nm. The spectra for samples prepared at substrate temperature from 240°C to 320°C are formed by a broad band with a maximum located at around 460 nm. However, this band has a shoulder located at 410 nm. For samples deposited in the range from 340°C to

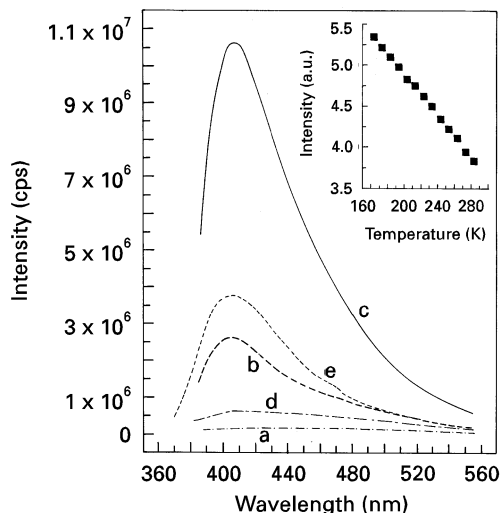


Fig. 3. Emission spectra for aluminium oxide films deposited at substrate temperatures of 240°C (a), 320°C (b), 380°C (c) and 440°C (d) using an organometallic compound as source material. The spectrum (e) corresponds to a sample deposited at 380°C using aluminium chloride as source material. All the spectra were obtained with an excitation wavelength of 371 nm.

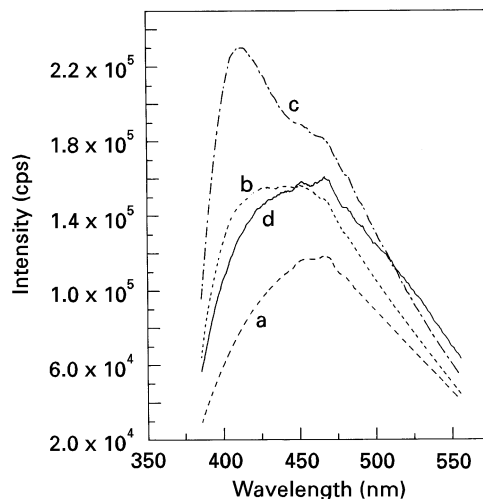


Fig. 4. Emission spectra for Al_2O_3 films deposited at 240°C (a), 320°C (b), 340°C (c) and 420°C (d) with a wavelength excitation of 281 nm.

400°C , this shoulder has higher intensity than the peak located at 460 nm. Meanwhile, for the samples with 420°C and 440°C , the PL spectra are similar to that obtained in samples with low

substrate temperature. From the measurements of the emitted light intensity as a function of the temperature, using the 371 nm excitation wavelength, see inset in Fig. 3, it is observed that the general form of the emission spectra does not change and the intensity increases only by a factor of 1.5 for the lowest temperature, indicating a relative small effect of the vibronic spectra on the emission transitions, as it is observed in luminescent centers having shielded energy levels, like rare earths with high quenching temperatures.

It has been reported a similar photoluminescent emission in anodic oxide films formed on aluminium in lower aliphatic carboxylic acid [19]. In that case, dissolution of oxalic acid films in 1 M sulphuric acid results in uniform pore widening throughout the oxide film and the determination of the distribution of incorporated impurities across the pore wall is possible by varying the dissolution time. The pore wall material was analyzed by means of photoluminescence measurements. The general form of the PL spectra is similar to these obtained in the present work, but in that case the maximum is located at about 470 nm, using excitation wavelength of 310 nm. However, this peak is shifted to lower wavelength depending on the dissolution time and, then its localisation depends on the chemical composition of the analyzed material. They suggest that the observed emission is associated with incorporated oxalate ions which are present in various states within the oxide. On the other hand, it was reported that rhombohedral aluminium oxide also shows a broad band photoluminescent emission with a maximum located at 300 nm [20]. In that case it was suggested that the luminescent centre is associated with an excess aluminium. Recently, it was reported the preparation of hydrated oxides, they were prepared boiling aluminium in ultra-pure water, after that the samples were annealed in forming gas at 780°C for a given time. A green/blue photoluminescent peak, around 2.8 eV, was found in ultra-pure alumina such that it was attributed to alanol groups (= Al–OH), in which the aluminium atoms attached to the OH groups have their highest oxidation state three [21]. The intensity of this peak depends on the alumina hydrated degree, with the highest intensity for an annealing temperature of 420°C. For anneal-

ing temperatures higher than 500°C, the photoluminescent emission vanishes and it is associated with desorption of isolated OH groups. In that case the absorption of UV light occurs in a wide band gap material, like defects in the alumina. Photogeneration of carriers associated with excitation from valence band to conduction band is excluded because the photon energy for excitation (3.65 eV) is smaller than the band gap of alumina. The photogenerated carriers are trapped in sites with a lower binding energy, such as alanol groups, where the photoluminescent emission occurs. However, they do not give any detailed microscopic mechanism of the OH related photoluminescence. On the other hand, the result from the relative chemical composition by means of EDS shows that only aluminium and oxygen are the constituent elements of the deposited films, within the detection limits of the technique. This fact permits to rule out the existence of zinc oxide nanocrystals in the films. All the spectra shown in Fig. 3 have similar form. These facts suggest that the photoluminescence, in the present work, must be associated with only one kind of luminescent centre which does not appear to be organometallic radicals or chlorine radicals incorporated in the films. On the other hand, in the present case the excitation peaks (3.35 and 4.43 eV), shown in Fig. 2, exclude the possibility that excitation of carriers can be achieved by valence band to conduction band transitions because the energies of these photons are smaller than the band gap of alumina. Then the absorption of UV light could be by defects in the alumina. The photogenerated electron might be trapped in an excited level associated with an aluminium ion where the photoluminescent recombination takes place.

Taking into account the result of the small effect of the vibronic spectra on the intensity of the emitted light, it can be considered that the spectra are composed of inhomogeneously broadened purely electronic transitions and then all the obtained spectra can be decomposed in several Gaussian distributions. If it is made, the deconvolution with a minimal of three components reproduce the spectra without deviations. It is well known that the reproduction of the spectra is also possible using a higher number of contributions, but in the present work it is considered that there is a good fit

taking into account only three contributions. Fig. 5 shows the emission spectrum for the sample prepared with organometallic source material at substrate temperature of 400°C. This spectrum can be decomposed using three Gaussian distributions as it is shown. The maximum of these contribution are located at (a, peak 1) 398, (b, peak 2) 417 and (c, peak 3) 449 nm, respectively. The sum of these three contributions (d) (dotted curve) is also shown. This deconvolution indicates that the broad band emission could be composed by at least three contributions which might be associated with both (i) three different luminescent centers or (ii) three radiative electronic transitions within the same luminescent centre. For the present case, if it is considered that the evolution of the microstructure and, mainly the accommodation of the aluminium atoms (given the refractive index values measured), change the local electric field on the aluminium atoms, as has been observed for metallic impurities in several glass materials [22,23], it is suggested that there is only one kind of luminescent center and the different contributions are explained by changes in the local electric field, which can change the intensities and positions of the emitted lines, because when an ion (metallic in the present case) is placed into a glass matrix, the ions surrounding the ion influence its

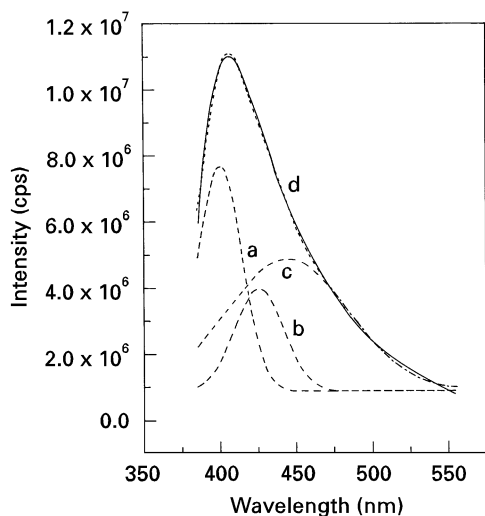


Fig. 5. Deconvolution in three Gaussian of the emission spectrum for the Al_2O_3 sample prepared at 400°C.

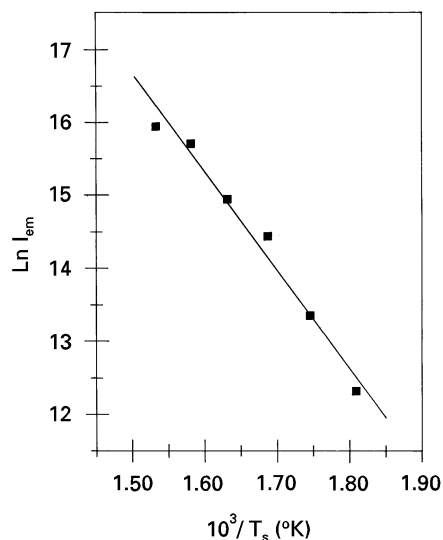


Fig. 6. Peak 1 intensity of the Al_2O_3 emission as a function of the inverse of the deposition temperature. The slope from a linear regression defines an activation energy of 1.16 eV.

energy levels giving place to the splitting of the levels into several components which are shifted and broadened [23]. On the other hand, it appears that the deposited material does not have a homogeneous composition which is due to the growth process. The obtained PL spectra for all samples show a similar behaviour. However, it is not possible to give a detailed model for the mechanism of the radiative recombination processes and of the photoluminescent centre.

Considering that the luminescent centres are uniformly distributed through the films and taking into account the differences in the films thickness, the maximum intensity of the first contribution (peak 1) was normalised for a film thickness of 100 nm, for all studied samples. Fig. 6 shows an Arrhenius plot of the normalised maximum of the intensity of peak 1 as a function of the substrate temperature. A linear behaviour for substrate temperatures from 280 to 380°C is observed. From a linear fitting, it is calculated that the activation energy to produce this luminescent center is 1.16 eV. From similar Arrhenius plots for peaks 2 and 3, with the same excitation wavelength, 371 nm, the activation energies calculated are 0.83 and 0.85 eV, respectively.

4. Conclusions

Aluminium oxide films deposited by the ultrasonic spray pyrolysis process, at substrate temperatures in the range from 240 to 440°C, show violet-blue photoluminescence emission under excitation of 281 and 371 nm wavelengths. The spray solutions were 0.05 M of: (i) aluminium acetylacetonate and (ii) aluminium chloride in a mixture of two parts of deionised water and two parts of methanol. The X-ray diffraction spectra obtained for all the samples indicate that the deposited materials are of amorphous nature. The ellipsometry measurements give refractive index values lower than those observed in crystalline Al₂O₃ phases. This behaviour is associated with (i) the amorphous nature, (ii) the incorporation of organic radicals or chlorine related radicals and (iii) the open microstructure of the deposited films. The photoluminescent centre is associated with an excess of aluminium ions instead of organic or chlorine radicals, alcohol groups or zinc oxide nanocrystals incorporated in the films. All the emission spectra are formed by a broad band which appears to be composed by, at least, three contributions and these contributions could be associated with three different accommodation sites of the aluminium atoms in the alumina matrix. An Arrhenius plot of the normalised maximum of the peak 1 as a function of substrate temperature gives an activation energy for the formation of the photoluminescent centre, of 1.16 eV. For a precise determination of the centre responsible for the observed photoluminescence, more work like: decay time, PL measurements using polarized light, temperature dependence of the emission down to 77 K, etc., should be made.

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