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Structural and Optical Characteristics of Gallium Oxide Thin Films Deposited by Ultrasonic Spray Pyrolysis

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Amorphous gallium oxide thin films were prepared by the ultrasonic spray pyrolysis method using gallium acetylacetonate as source material and water as oxidizer. Samples annealed at 850°C during 1 h show the crystalline β-phase of Ga_2O_3. Rutherford backscattering results indicate that both as-deposited and annealed films have the stoichiometric chemical composition without incorporation of carbon impurities. Infrared (IR) spectroscopic measurements show that there is no incorporation of O-H and Ga-OH radicals in any of the studied films. The IR spectra for amorphous films show a broad absorption band from 400 to 900 cm^{-1}, typical for some amorphous metallic oxides. Meanwhile, for the annealed films the IR spectra show well-defined peaks located at 450 and 670 cm^{-1} related to the β-phase of Ga_2O_3. The refractive index of the films shows a strong change from 1.846 for the amorphous films to 1.935 for the annealed ones. The optical bandgap energy values are 4.94 eV for the as-deposited films and 4.99 eV for the annealed films. All these changes are associated with a different microstructure of the annealed films.
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Gallium oxide can have several crystalline phases, such as α, β, γ, σ, and ε type. Among them, the β-Ga_2O_3 modification, monoclinic, is the only phase which is thermally and chemically stable at temperatures up to its melting point (1800°C).[1] This phase is normally an insulating material at room temperature with a bandgap energy of about 4.9 eV. Due to its optical and electrical properties, gallium oxide has been applied in metal-insulator-semiconductor structures.[2] This material shows a semiconducting behavior at temperatures higher than 500°C. The n-type semiconducting property is associated with a slight oxygen deficiency in the crystal lattice. The top of the valence band of β-Ga_2O_3, which contains two crystallographically different Ga atoms,[3] is formed by nonbonding 2p oxygen orbitals, while the bottom of the conduction band is predominantly constituted of 4s octahedral gallium orbitals, without contribution of atomic orbitals from tetrahedral gallium ions.[4] On the other hand, when gallium oxide is prepared under reducing atmosphere it behaves like an n-type semiconductor due to the resulting gallium excess or oxygen deficiency in the crystalline structure.[5] Electrons in the introduced donor states are responsible for the blue luminescence observed in this phase, which is characterized by strong electron-phonon coupling.[6]

Recently a renewed interest in β-Ga_2O_3 has arisen for applications as transparent conducting contact in optoelectronic devices,[7] oxygen sensors at high temperatures (≅900°C), and reducing gas sensors at relatively low temperatures (<700°C).[8] The use of stable metallic oxides as gas sensors at high temperatures has several advantages, such as short response time and simple conduction mechanism.[9]

Gallium oxide thin films have been prepared by high-frequency sputtering, electron-beam evaporation, chemical vapor deposition, and atomic layer epitaxy (ALE).[10-13] In general, films deposited by these techniques are amorphous, and in several cases, they result with incorporation of carbon impurities coming from the used gallium source material. There are, also, reports on the preparation of gallium oxide films by means of the spray pyrolysis method with ultrasonic nebulization, using $GaCl_3$ and $Ga(NO_3)_3$ as source materials of gallium.[14,15] Probably the pyrosol process is the easiest and lowest cost nonvacuum technique to prepare thin films over large areas. Thin films prepared by this process show homogeneous properties on areas with adequate size for gas sensor applications (≈0.5 × 0.5 cm).

In this work we report on the preparation and characterization of gallium oxide films by the pyrosol process using commercial gallium acetylacetonate as source material. The gallium acetylacetonate is inexpensive, nontoxic, and stable in an air atmosphere at room temperature. The structural characteristics of both amorphous and crystalline Ga_2O_3 films were investigated by Fourier transform infrared spectroscopy (FTIR) and refractive index measurements. Ellipsometry and IR transmission are simple techniques which have been successfully used to study the structure, chemical composition, and hydrogen content of other oxide films such as SiO_2. However, to our knowledge, similar studies have not been realized earlier in Ga_2O_3 films.

Experimental

Gallium oxide thin films were deposited by the ultrasonic spray pyrolysis method. There are several reports where the ultrasonic spray pyrolysis, also called pyrosol process, has been explained in detail.[16] It has been proven that with this low-cost process it is possible to prepare thin films with uniform thickness and chemical composition if the geometry and deposition parameters are carefully adjusted. We have previously controlled these aspects in our pyrosol system to prepare uniform films of insulating and luminescent materials.[17-19] The starting solution was 0.05 M of gallium acetylacetonate (GAAc) dissolved in a mixture of 1 part deionized water and 1 part methyl alcohol. Glacial acetic acid was added (5 mL/L) to obtain a complete dissolution of the source material. In general, it is known that organometallic compounds have suitable thermodynamic and chemical properties to ensure a vapor phase chemical reaction.[20] The samples were prepared at substrate temperatures in the range from 300 to 500°C in 25°C steps. Filtered air was used as carrier and director gas, the air flow rates were 3.5 and 0.5 L min^{-1}, respectively. The deposition time was varied from 15 to 30 min. The shortest time was used for the lowest substrate temperature, and the longest time was used for the highest substrate temperature used in this work. These combinations of substrate temperature and deposition time were chosen to compensate for the effect observed in thin films deposited by spray pyrolysis that for a constant deposition time, film thickness decreases as the substrate temperature increases.[21] In this way a similar thickness was obtained for all the deposited films. In order to promote crystallization of the films, samples prepared at substrate temperature of 350°C were annealed at temperatures of 850, 900, and 925°C, in air atmosphere, during 1 h. In order to check the effect of the annealing time on the final crystallinity some of the films were annealed at 925°C during 0.5, 2, and 3 h. The substrates used for X-ray diffraction (XRD) and optical transmission measurements were clear fused quartz slices, which were ultrasonically cleaned with trichloroethylene, acetone, and methanol prior to deposition. For profilometry measurements, Pyrex glass slices, cleaned in a similar way as the above mentioned case, were used as substrates. During deposition a small part of these

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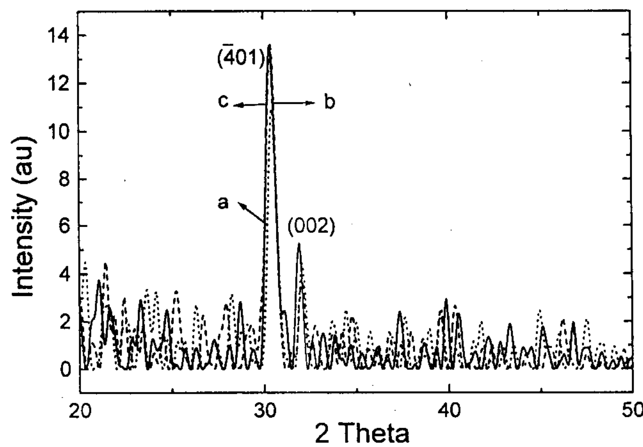

Figure 1. XRD spectra from a Ga_2O_3 film, deposited at 350°C on clear fused quartz substrates, annealed at (a) 850, (b) 900, and (c) 925°C in air during 1 h.

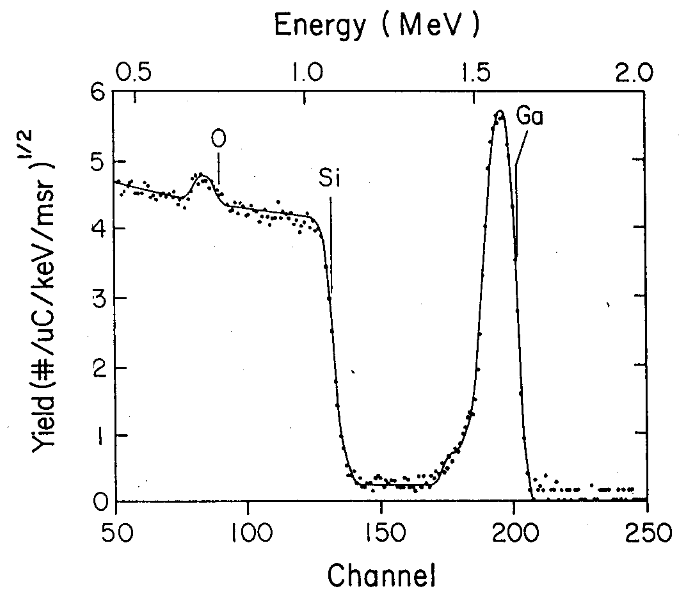

Figure 2. RBS spectrum for a gallium oxide film deposited at 350°C and annealed at 850°C during 1 h. No signal related with incorporated carbon is observed.

substrates was covered with a cover glass slice to get a step. For ellipsometry, IR spectroscopy and elemental composition measurements (100) n-type silicon single-crystal wafers with 200 Ω cm were used. The native oxide was remove from the c-Si wafers by wet chemical etch with P solution (15 parts of HF, 10 parts HNO_3, and 300 parts H_2O).[22] The structure of the as-deposited and annealed samples was analyzed by means of XRD measurements with a Siemens D5000 diffractometer. The elemental composition and the atomic density (atoms/cm^2) of the as-deposited and annealed gallium oxide films were obtained using the ion beam analysis (IBA) facilities at the University of México based on a vertical single-ended 5.5 MeV Van de Graaff accelerator.[23] It is known that IBA methods also allow determination of the depth profile of the constituent elements. A conventional Rutherford backscattering technique with a 2 MeV $^4He^+$ beam with detector set at $\theta = 170°$ was used to analyze the films. A surface barrier detector and standard electronics were used to obtain the particle energy spectra. The thickness of the films was measured with a Sloan Dektac IIA profilometer on the step formed during deposition. The refractive index and the thickness of the films were measured with a Gaertner 117A ellipsometer using the 632 nm line from a He-Ne laser. Infrared (IR) transmittance measurements were made with a FTIR 210 Nicolet spectrophotometer. Optical transmission measurements, in the range 190-1100 nm, were carried out with a double-beam Shimadzu UV-visible 260 spectrophotometer with air in the reference beam.

Results and Discussion

The thickness of deposited films was around 89 nm with deposition rates between 30 and 60 A/min, depending on substrate temperature. The as-deposited samples were of amorphous nature as observed from their XRD spectra. However, the annealed samples show a polycrystalline microstructure as observed in Fig. 1 for films annealed at (a) 850, (b) 900, and (c) 925°C during 1 h. It should be verified that the films did not flake off or crack after annealing. The XRD spectra, using an X-ray wavelength of 1.5418 A, for all these annealed samples correspond to a monoclinic crystalline structure (ASTM card 41-1103). This structure is identified as the β phase of Ga_2O_3, which is the stable phase at high temperatures. It appears that these spectra show a preferential orientation of the crystalline structure because in all of them there is a dominant peak associated with reflection in the ($\bar{4}01$) family of planes. Similar XRD spectra were obtained for the samples annealed at 925°C with different annealing times. These results indicate that there is no strong difference in the magnitude of the reflection peaks as a result of the different used values of temperatures and annealing times. XRD spectra for films with thickness of 500 nm and annealed at 850°C show that the magnitude of the reflection peaks depends on the thickness of the films. The grain size for these films and for those thinner films (thickness ≅ 89 nm), calculated by means of the Scherrer formula, have similar values. It appears that the annealing process does not promote a large grain growth and their values are not restricted by the thickness of the films. The weak effect of the annealing process on the grain growth is due to the relatively low annealing temperature (850°C). It has been observed that to get a large grain growth the annealing process should be carried out at temperatures of the order of 1100°C for 50 h.[24]

Figure 2 shows a typical backscattered $^4He^+$ spectrum of 2 MeV ions incident at 0° angle with respect to the normal of the gallium oxide films deposited on silicon substrate at 350°C and annealed at 850°C. In this spectrum signals associated with gallium, silicon, and oxygen can be observed. It should be noted that as-deposited films give similar spectra. In all analyzed samples no signal related with incorporated carbon, as a residual by-product of the chemical reaction, was observed. This is an interesting result considering that amorphous gallium oxide films prepared by ALE using GAAc and water as the oxidizer have carbon impurity content of 30 atom %. The carbon content in those films can be reduced to levels as low as 1 atom %, but only if ozone is used as the oxidizer agent.[13] Residual incorporated carbon is also observed in films prepared by chemical vapor deposition (CVD) using gallium trishexafluoroacetylacetonate as gallium source material.[11] A quantitative analysis of the Rutherford backscattering (RBS) spectra was made using the well-known "RUMP" software.[25] The analysis consists of a simulation of the spectrum (solid line) and its comparison with the experimental one (dots). Figure 3 summarizes the RUMP depth profile used to generate the RBS spectrum. Three layers were needed to simulate the spectrum. The first (front) layer is a stoichiometric Ga_2O_3 homogeneous film with an areal density of 700×10^{15} atoms/cm^2. The second and third layers form a thick interface region, which shows that Ga and O are diffused into the silicon substrate. The diffusion of oxygen into the crystalline silicon substrate and the consequent formation of thermal SiO_2 is well expected given the high annealing temperature used in the present work.[26] The RUMP errors for the oxygen and gallium concentration determination are about 8%.

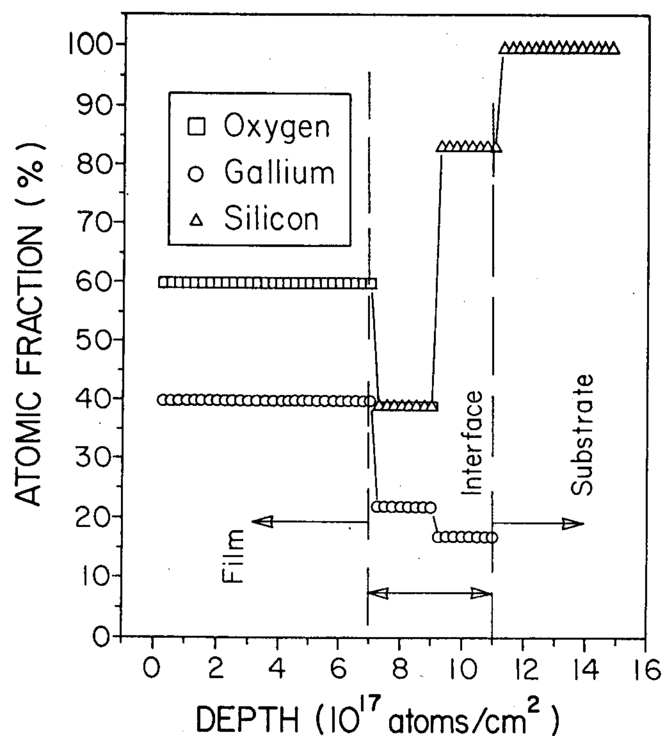

Figure 3. Depth profile concentration for a gallium oxide film annealed at 850°C. It can be observed that the film is formed by stoichiometric Ga_2O_3 material.

Figure 4 shows that the refractive index for the as-deposited films takes values in the range 1.846-1.864. These values are lower than that associated with bulk gallium oxide (1.92-1.95),[27] which is reasonable considering that the as-deposited films are amorphous and consequently, they do not have a compact structure. In Fig. 4 it is observed that the refractive index, for the as-deposited films, has a maximum value at a substrate temperature of 425°C. This fact is explained considering that at low substrate temperatures the deposited material results in an open microstructure due to the low surface mobility of the adsorbed species during growth. At Ts = 425°C, the surface mobility of the adsorbed species is increased, resulting in a less open microstructure. However, it is not high enough to get a crystalline phase. The lower refractive index values for the samples deposited at substrate temperatures higher than 425°C are explained taking into account that at those Ts, chemical reactions in gaseous phase near the surface of the substrate are possible, leaving powder particles incorporated in the film resulting in films with high porosity. The refractive index for annealed films takes higher values, which varies in the range from 1.920 to 1.935. This change in the refractive index value, in comparison with that of the as-deposited films, is explained by the crystalline nature of the annealed films which have a more compact microstructure. The results of the crystallinity and refractive index for the annealed films indicate that the annealing treatment produces crystallization of the material. The thickness values of deposited films were around 89 nm with a deposition rate that depends on the substrate temperature. These deposition rate values (≈30-60 A/min, depending on Ts) are higher than those obtained in gallium oxide films deposited by ALE using GAAc (≈15 A/min), although the refractive index has similar values (1.8-1.9).[13] Although the deposition rate in the ALE process is lower than the value obtained in the present work, the refractive index values are still similar because film deposition in the ALE process was achieved by introducing the reactants alternately in the reactor using nitrogen as purging gas. Meanwhile in the present case the gallium source material (GAAc) and the oxidizer agent (water) were used, forming a liquid solution.

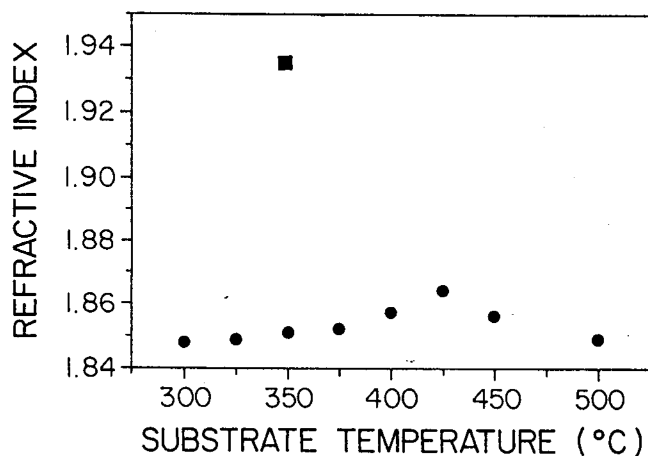

Figure 4. (●) Dependence of the refractive index as a function of the substrate temperature for as-deposited Ga_2O_3 films. (■) The refractive index for a film annealed at 850°C in air atmosphere.

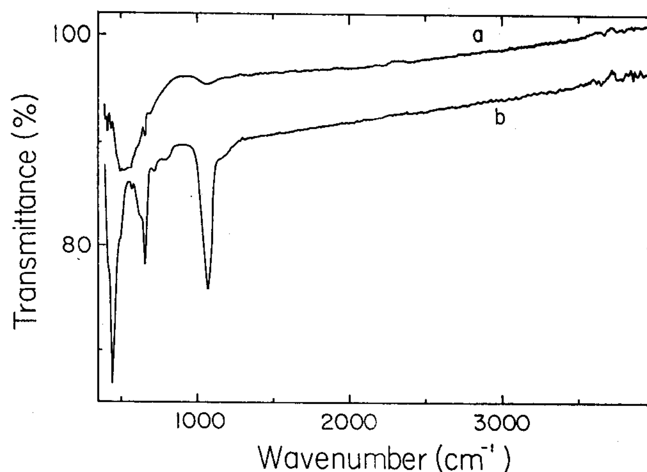

Figure 5. IR transmittance spectra for (a) a Ga_2O_3 amorphous film deposited at 350°C and (b) a Ga_2O_3 polycrystalline film.

Figure 5 shows the IR spectra obtained for an as-deposited sample prepared at a substrate temperature of 350°C (a) and for a film annealed at 850°C. The spectrum from the as-deposited sample shows a broad absorption band located in the range from 400 to 900 cm^{-1}, which is associated with the amorphous nature of the as-deposited material. Similar results have been observed in other amorphous metallic oxides prepared by several techniques.[28] A small peak is also observed at around 1070 cm^{-1}, which can be clearly identified with the stretching vibration mode of the Si-O bond.[29] This result is in agreement with the results obtained from IBA measurements, where silicon and oxygen are detected in the interface zone. Both results indicate that silicon dioxide is formed at the interface between the c-Si substrate and the deposited material during film growth. The IR spectrum for the annealed film (Fig. 5b) shows two well-defined peaks instead of the broad band observed in the as-deposited sample. The observed peaks are located at 450 and 670 cm^{-1}, which are related with the crystalline nature of annealed films (β phase of the gallium oxide). The locations of these peaks are in agreement with wavenumber values published earlier.[30] However, to the knowledge of the authors, the corresponding vibration modes of the Ga-O bond have not been identified yet. The magnitude of the absorption peak related to the stretching vibration mode

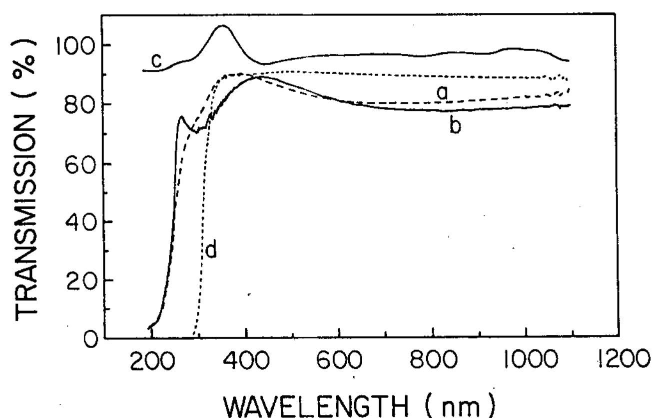

Figure 6. Optical transmission for (a) as-deposited and (b) annealed Ga_2O_3 films, and the spectra for (c) clear fused quartz, similar to that used as substrates, and for (d) a nude Pyrex glass slice.

of the Si-O bond is increased by the annealing process. This confirms that at the annealing temperature used in this work, there is growth of a silicon dioxide film.[26] It is important to note that for annealed samples, and even for the as-deposited films, there is no signal related with the existence of O-H radicals. This fact permits the inference that there are no Ga-OH radicals incorporated in the prepared films. These results could be important from an electrical point of view, because the O-H radicals act as charge carrier traps. Similar results were obtained for all the as-deposited and annealed samples.

Figure 6 shows the optical transmission spectra for (a) an as-deposited sample, (b) an annealed sample at 850°C, and (c) a clear fused quartz slice similar to those used as substrates. From the data of the optical transmission as a function of the photon energy, the energy bandgap calculated in these cases was 4.94 eV for the as-deposited film and 4.99 eV for the annealed sample. These values were obtained using the Manifacier method,[31] which has been applied to wide bandgap metallic oxides considering direct allowed optical transitions. It can be observed that there are no strong changes in the location of the absorption edge for amorphous and the crystalline β-phase of gallium oxide. Similar results were obtained for all the studied samples. The energy bandgap values obtained are in agreement with those reported earlier.[15] The reported value of 4.25 eV[14] should be related to the absorption edge of the glass substrates used in that work, since that result is similar to the one obtained in the present work for naked glass, as shown in Fig. 6d.

Conclusions

The as-deposited gallium oxide films prepared by ultrasonic spray pyrolysis are of amorphous nature. However, annealing of these samples at temperatures in the range from 850 to 925°C and annealing times from 0.5 to 3 h results in the crystalline β-phase of gallium oxide. IBA shows that as-deposited and annealed films have a stoichiometric chemical composition. The refractive index changes from 1.838 for as-deposited samples to 1.95 for annealed samples. The IBA results show that there is no signal of carbon incorporation. The annealing process also changes the IR absorption spectra. The as-deposited films show a broad band located in the range from 400 to 900 cm^{-1}, whose general form appears typical for amorphous metallic oxides. The IR absorption spectra of annealed films show two well-defined peaks related with the crystalline nature of β-phase of gallium oxide. It was found by these studies that even amorphous Ga_2O_3 films prepared at the lowest temperatures by the pyrosol process are free of O-H or H_2O. A clear correlation was also found between variation in the refractive index and IR features as the structure of the Ga_2O_3 films changes from amorphous to crystalline. A silicon dioxide interfacial layer between the c-Si substrate and the gallium oxide films is promoted by the annealing process. The gallium oxide films show direct allowed optical transition with energy bandgap values of 4.94 eV for amorphous films and 4.99 eV for annealed films. There are no strong changes in the optical absorption edge for the as-deposited and the annealed films.

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