Effect of Au/SiO₂ substrate on the structural and optical properties of gallium nitride grown by CVD

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Abstract. The improvement of the growth of thick GaN films using a fused silica wafer covered with a thin gold layer by chemical vapour deposition at 800 °C is reported. In order to compare the surface properties, crystalline quality, micromilling performance and luminescence, the characterization of a GaN film grown on a silicon wafer is presented as well. The different morphologies of the surface observed on the GaN films are compared on each substrate and the resulting microstructures are presented in detail. High resolution TEM images of the GaN films show the main crystallographic planes characterizing these structures. The wurtzite structure was determined for each sample using the substrates of Au/SiO₂ and Si (100) from the XRD patterns. Also, the re-deposition effect after ion milling of the GaN films is reported. The performance of ionic beam on the surface of the GaN thick films for the geometries patterning of rectangular, circular and annular with two different ion doses was compared. Cathodoluminescence spectra showed that the top surfaces of the samples emit strong UV emissions peaked at 3.35 and 3.32 eV which are related to the Y₄ and Y₆ transitions.

Keywords. Gallium nitride; gold layer; fused silica; silicon; substrate.

1. Introduction

Gallium nitride (GaN) and their alloys (InGaN–AlGaIn) have found important applications due to their broad band gap (3.4 eV) suitable for high power electronics, light emitting diodes, sensors and solar cells (Hwa-Mok *et al* 2004; Dong *et al* 2009; Chen *et al* 2012; Chang-Ju *et al* 2013). Initially, the gallium nitride was developed as powder material but the development of their applications in optoelectronics gradually decreased the attention of researchers.

The technical difficulties inherent to the handling as a powder and the control of their physicochemical properties, allowed the development of thick or thin films of these compounds, which was more practical and reproducible. As a result, GaN has established more remarkable results on films technology and their wide expansion into the optoelectronics devices at blue and ultraviolet wavelengths (Li *et al* 2006; Sun *et al* 2010).

Currently, the high-quality GaN films have been grown through several techniques such as metal–organic chemical vapour deposition (MOCVD) and molecular beam epitaxy (MBE) (Hughes *et al* 1995; Chul-Woo *et al* 1999; Martinez-Criado *et al* 2000; Hersee *et al* 2006; Thillozen *et al* 2006;

Richter *et al* 2008; Sobanska *et al* 2012). By means of these growth methods, the improvement of luminescence efficiency in the GaN-based devices was characterized on various substrates. Despite of the high dislocation density obtained, the quality of GaN has been improved using the sapphire substrate. However, the search of a suitable substrate for this nitride is still in discussion and other candidates have been proposed for GaN epitaxy such as ZnO, β -SiC, BP, GaAs, GaP, Si, MgAl₂O₄, MgO, γ -LiAlO₂, ZrN, ScN and TiN (Liu and Edgar 2002).

Besides of the research on the growth techniques for the gallium nitride, the influence of the substrate on the crystalline, electron, optical and compositional properties of the GaN deposition is still in discussion, which motivates to discover new routes to improve the quality of gallium nitride films. The present work reports the results on the surface morphology, crystalline structure, milling pattern and optical emission of GaN films grown by chemical vapour deposition at 800 °C. To compare the GaN properties under different substrates, a fused silica wafer covered with a thin gold layer (Au/SiO₂) and a wafer of monocrystalline silicon (Si) are used. Using scanning electron microscopy (SEM), the formation of segregates and irregular polyhedral in the surface of GaN films on the substrates of Au/SiO₂ and Si were found. By means of transmission electron microscopy (TEM), high

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Figure 1. Schematic diagram of the CVD horizontal reactor used for the growth of GaN films on Au/SiO₂ and Si substrates.

resolution images and interplanar distances were obtained for GaN films. To study the crystalline structure, X-ray patterns were analysed for both samples and their average grain size was calculated from X-ray diffraction (XRD) experimental data. In order to characterize the gallium nitride films with regard to the probability of forming submicron structures, 2D milling patterns were performed by using focus ion beam (FIB). Two broad emissions peaked at 3.35 and 3.32 eV related to the Y₄ and Y₆ transitions were obtained in the GaN films by cathodoluminescence (CL).

2. Experimental

Thick GaN films under study were grown by chemical vapour deposition at 800 °C on two different substrates: (i) a fused silica wafer covered with a gold layer (Au/SiO₂) and (ii) a silicon wafer. Figure 1 presents a schematic diagram of the CVD system showing the main zones and set up of the growth process. The CVD system consists of a horizontal quartz tube of 2½" diameter divided in three zones. Additionally, two concentric tubes of ¾" diameter were used for the introduction of high purity ammonia (NH₃) and nitrogen (N₂) as carrier gases. Two containers with ammonia chloride salt (NH₄Cl) and metallic gallium (Ga) are located at the entrance of the zone 1 and the middle of the zone 2 of the CVD system, respectively. The GaN deposition on the substrate occurs based on the decomposition of NH₄Cl and the formation of volatile chloride (GaCl) compound (Garcia *et al* 2008; Ramos-Carrasco 2013). The growth process for the deposition of GaN on both Au/SiO₂ and Si substrates was performed at atmospheric pressure using a nitrogen flux of 200 sccm and an ammonia flux of 300 sccm.

Two types of substrates based on amorphous and crystalline materials were used for the growing process of GaN films by means of the CVD method. Both substrates were treated with a chemical cleaning solution using an ultrasonic bath of 35% hydrofluoric acid to remove impurities. After that, a thin Au layer of approximately 50 nm was deposited on a fused silica wafer of 25.6 mm diameter by means of sputtering. For the second sample, a silicon wafer of 50 mm diameter with a resistivity of 1–10 Ωcm^{−1} was used as substrate. Before the deposition, each substrate was placed in

zone 2 and a heat treatment was applied at 800 °C for 1 h under vacuum conditions.

The morphology of the surface of GaN films was obtained by means of a JEOL 5300 scanning electron microscope. Also, the root mean square (rms) roughness of gallium nitride films was measured using a JSP-4210 JEOL atomic force microscope (AFM). High resolution images were recorded in a Tecnai Philips F20 transmission electron microscope. The XRD patterns were performed with a D500 Siemens diffractometer in a range of 20–70° (2θ) at room temperature using a wavelength of 1.54 Å, at 45 KV and 30 mA. The 2D patterns were obtained in a multibeam JIB-4500 focus ion beam with doses of 10 and 5 nC/μm² and a voltage acceleration of 30 KV. The cathodoluminescence spectra of the GaN films were recorded in a JEOL JSM 6300 SEM with a voltage acceleration of 5 KV and current of 300 pA at room temperature.

3. Results and discussion

Figure 2 shows the SEM images of the GaN thick films grown by chemical vapour deposition during 60 min on Au/SiO₂ and Si substrates. The formation of multiple segregates with a diameter between 1 and 10 μm were obtained in the GaN film using Au/SiO₂ substrate, as is presented in figure 2(A). The surface in a coalescence stage is related to the use of the gold layer and the formation of droplets after annealing, which promote the solid–liquid–vapour mechanism in the GaN film. To analyse GaN segregates, an energy dispersive X-ray spectrum was performed and absence of oxygen or pure metals was found. From figure 2(B), a uniform thickness of 5 μm of the GaN film grown on Au/SiO₂ substrate is presented by means of a cross-section SEM image. For the silicon substrate, an increment of the size of GaN structures was obtained without larger accumulations, as shown in figure 2(C). This film exhibits irregular polyhedra with hexagonal and triangular formations with diameters and facets lengths from 1 to 5 μm respectively. However, the top facet of the triangular shape was only observed for small crystals, while the hexagonal shape was observed on larger crystals. This phenomenon has been also reported on the growth of GaN nanoislands on Si-rich SiN_x and is

Figure 2. Plane-view SEM images of polycrystalline gallium nitride films grown on (A) Au/SiO₂ and (C) Si substrates. Cross-section images and estimated thickness of the GaN layers deposited on (B) fused silica and (D) silicon substrates.

Figure 3. AFM images illustrating the morphology surface for (A) GaN grown on Au/SiO₂ substrate and (B) GaN grown on Si substrate. Scan size of $5 \times 5 \mu\text{m}$.

related to the change of the island size and the annealing of the nucleations layers (Fang and Kang 2007). In comparison with the GaN grown on the Au/SiO₂ substrate, the thickness of the GaN film on Si is highly asymmetrical and porous with a maximum width of $5 \mu\text{m}$ approximately, as shown in figure 2(D). Figure 3 shows atomic force microscopy measurements were used to obtain the surface morphology. For gallium nitride deposited on Au/SiO₂ substrate ($5 \times 5 \mu\text{m}^2$) a rms roughness of 156 nm in the surface was obtained while the nitride grown on silicon wafer shows an increment in the roughness of 274 nm.

Figure 4 presents two high resolution TEM images of GaN films grown on Au/SiO₂ and Si substrates. For the first sample, the crystallographic plane (002) was identified and indexed using the corresponding interplanar distance of the

gallium nitride according to the ICDD card database 00-050-0792, as shown in figure 4(A). From figure 4(B), the diffraction pattern showing a hexagonal shaped geometry with three crystalline orientations related to the crystallographic planes (100), (002) and (101) was obtained in the GaN film grown on silicon substrate.

Figure 5 contains the XRD patterns obtained in GaN films grown on Au/SiO₂ and Si substrates. The θ - 2θ scan confirms that both GaN films present a wurtzite crystalline structure according to the ICDD card database 00-050-0792. Figure 5(A) displays the single XRD peak obtained in the thick GaN film using the Au/SiO₂ substrate at $2\theta = 34.3^\circ$ corresponding to the (002) *c*-plane. No other crystalline phases were present as shown in the XRD characterization for this GaN sample, either such as pure metals or oxides.

Figure 4. High-magnification TEM images (A and C) and crystallographic planes (B and D) observed in the GaN crystallites grown on Au/SiO₂ and Si substrates.

Figure 5. XRD patterns of GaN films obtained by chemical vapour deposition at 800 °C using two different substrates.

Figure 5(B) shows the XRD pattern of the gallium nitride grown on Si wafer, showing one intense diffraction peak at 34.7° and five weaker peaks at 32.6, 37.1, 48.2, 63.3 and 69.3 (2θ) degrees corresponding to (002), (100), (101), (102), (103), (112) planes, respectively. The high intensity of the XRD peaks from the *c*-plane on both GaN films demonstrates the preferential direction orientated in the basal plane. However, the fact that the GaN grown on Au/SiO₂ appears to suppress the rest of the crystallographic planes, suggest a good control of crystalline quality because of the gold layer. Establishing as reference, the *c*-plane (002) for both samples, through the full width at half maximum (FWHM) corresponding to every sample, the mean crystallite size was calculated for GaN films using the Scherrer equation. For the gallium nitride grown on Au/SiO₂ substrate, the average crystal size was 1.5 nm while for the specimen grown on Si substrate, their crystal size was about 1.1 nm. From these results, the quality of the GaN deposited on crystalline

silicon is comparable to that obtained on fused silica covered with a gold layer.

Figure 6 presents four 2D patterns produced on the surface of GaN films by means of focus ion beam. A rectangular milling ($10 \times 2 \mu\text{m}$) applied to one GaN segregation obtained on the Au/SiO₂ substrate using a dose of $5 \text{ nC}/\mu\text{m}^2$ is shown in figure 6(A). Despite the emergence of GaN spheres, the segregated one exhibits a superficial level with respect to the GaN film which is sensitive to low dose of the ion beam. In order to establish a comparison, a circular milling (radii = $5 \mu\text{m}$) was produced selecting other GaN sphere, but using an increment of the dose up to $10 \text{ nC}/\mu\text{m}^2$, as presented in figure 6(B). As a result, the complete ablation of the GaN segregation was obtained with some re-deposited zones around the devastated area. From figure 6(C), a milling pattern ($10 \times 2 \mu\text{m}$) for the GaN film grown on silicon substrate with a dose of $10 \text{ nC}/\mu\text{m}^2$ is presented. For this rectangular geometry, a well-defined pattern with low

Figure 6. Secondary electron images showing FIB 2D patterns applied to the segregates and coalescing surface in the GaN films. (A) Rectangular and (B) circular patterns with doses of 5 and 10 nC/ μm^2 performed on Au/SiO₂ substrate. (C) Rectangular and (D) annular patterns realized on Si substrate.

re-deposition zones at the edges was obtained. To evaluate the damage of the surface on this GaN film, a different milling pattern with an annular (20 μm of external diameter) geometry was achieved, as demonstrated in figure 6(D). From these results, it becomes evident that gallium nitride grown on silicon wafer presents lower material re-deposition around the patterns, even with larger milling sections. Although, this work is focused on the comparison of two different substrates on the growth of GaN films, this characteristic issue should be studied profusely to expand the knowledge in the fabrication of patterned masks.

Figure 7 exhibits the CL spectra of GaN films grown on Au/SiO₂ and silicon substrates at room temperature. The Y₄ line emission of approximately 370 nm (3.35 eV) at 300 K was obtained in the GaN film grown on Au/SiO₂. Commonly, this peak is related to excitons bound to structural defects at the surface on undoped GaN. However, for this GaN sample the Y₄ emission presents a FWHM with higher value of 20 meV which exceeds previous reports. On the silicon substrate, a broader peak with higher intensity at 373 nm (3.32 eV) was obtained in the GaN film. In this case, this optical transition is known as the Y₆ line emission and has been associated with a surface donor–acceptor–pair (DAP). Also, this luminescence band is only reported for

Figure 7. The CL spectra of the GaN films deposited on (A) Au/SiO₂ substrate and (B) Si substrate.

undoped gallium nitride and is typical of films consisting in roughened surfaces.

4. Conclusions

In summary, GaN films were grown by chemical vapour deposition on fused silica covered with a thin gold layer

and also over silicon substrates. For Au/SiO₂ wafer, a decrease of the roughness in the GaN surface with multiple accumulations was obtained, while in crystalline silicon, the formation of irregular polyhedra was observed. Structural analysis of GaN films by means of XRD and TEM shows that the use of a thin Au layer on SiO₂ substrate benefits the crystalline growth of the GaN film, despite the amorphous nature of fused silica. Also, the Au/SiO₂ substrate improves the orientation growth on the GaN towards the *c*-axis and competes with the crystalline quality obtained in the GaN film deposited on the Si substrate. From the 2D milling patterns, the silicon substrate demonstrates a decrease of the re-deposition effect on the GaN film after ionic ablation. By using FIB milling, a low depth level of segregations on the surface was found and large quantities of re-deposited material were obtained in the film grown on Au/SiO₂ substrate. CL measurements for GaN films show an emission with higher energy for the sample grown on Au/SiO₂ than that obtained on silicon with a slight decrease on the intensity. The Au/SiO₂ substrate reported in this work demonstrates the properties of high crystalline quality and optical emission of a GaN film, which also are comparable with the obtained results in the specimen grown on the Si substrate.

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