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Synthesis and characterization of gallium nitride nanoparticles by using solvothermal-soft-chemical methodology

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ABSTRACT

GaN nanoparticles have been synthesized by solvothermal method. Gallium acetylacetonate and ammonium acetate were mixed in stoichiometry conditions. The reaction was induced in different solvents such as ethanol, ethylene glycol, propanol and benzene. The as-prepared materials were heat-treated from 240 to 950 °C. X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) put in evidence that the resulting intrinsic-structure is highly linked with the solvent in turn and with temperature. It was found that wurzite phase is reached at 950 °C with benzene as a solvent; with surface area of 50 $m^2 g^{-1}$, measured by nitrogen physisorption. In addition, well-defined GaN-nanoparticles were determined using SEM–EDS and HRTEM for a diffraction-selected area (SAED). Moreover, optical properties obtained by using photoluminescence (PL) spectroscopy indicated a well crystal-definition from bands at 2.85 and 3.0 eV related with structural defects. GaN deposited onto an ITO substrate induced a more cathodic current corresponding to hydrogen evolution compared with ITO free of GaN in neutral conditions.

1. Introduction

The gallium nitride (GaN) physicochemical properties make this non-oxide compound an interesting material for application in optical and micro-electronics [1]. However, its advantages are even more important because the covalent bond between gallium and nitrogen enables its use in power electronics applications (e.g. high frequency transistors) where the abilities to dissipate a large amount of heat and to function in a high chemical activity environment are required [2,3].

Wurtzite, blend and sodium chloride are the three polymorphs of GaN. The wurtzite-hexagonal phase is thermodynamically stable with band-gap energy of 3.39 eV [4], emitting in wavelengths from blue to near ultraviolet light in electronic devices and violet light in diodes [1]. In addition,

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the probability for optical transitions increases due to its direct-gap intrinsic properties. Therefore, gallium nitride, which is linked with other elements from group IIIA, can be used in many applications due to its remarkable spectra from ultraviolet to infrared region [5].

In general, GaN has been prepared via a solid-state route using Ga_2O_3 as precursor in NH_3 atmosphere and 950 °C [6]. However, the use of different gallium precursors, such as GaAs and GaOOH in the presence of ammonia, has been reported more recently [7]. On the other hand, the growth of this non-oxide compound can only be performed with very specific materials, such as sapphire [5]. Moreover, different physical methodologies have been developed for material growth including physical vapor deposition, molecular beam epitaxy, arc discharge, and magnetron sputtering. According to the characterization results from scanning electron microscopy, interesting morphologies (i.e., nanowires, nanorods, nanobelts) have been observed on the micrometric level. Nevertheless, these routes are not designed for the preparation of GaN under mass scheme and technology that is friendly with the environment [8]. Therefore, in the previous years, new synthesis routes using soft chemistry have been studied as an alternative to replace the high-energy consumption approaches. Soft chemistry means to implement other methods for promoting chemical reactions (i.e., pressure, ultrasound, and microwave) to guarantee the physicochemical and optical properties at nano-metric scale resulting in a product suitable for use as a material in emerging areas, such as energy generation using renewable resources.

According to Zhu, only one-tenth of investigations related with semiconductors are focused on the nitride family and its different anions, and an exponential growth in the use of this material is predicted in the next 10 years [9–11]. Then, the development of sustainable methods for large-scale materials production is required. This study reports the synthesis of GaN using soft chemistry routes at low temperature and provides the corresponding physicochemical and electrochemical characterization associate with hydrogen production.

2. Experimental section

2.1. GaN synthesis

Gallium nitride was prepared by solvothermal route using gallium acetylacetonate (Aldrich, 99.99%) and ammonium acetate (Aldrich, 98%) as precursors in a stoichiometric relationship. In addition, in this work, different compounds, such as ethanol, ethylene glycol, propanol and benzene, were used as solvents (see Table 1). Each solvent was mixed in a 9:1 volume ratio with isopropanol (OmniSolv, 99.98%) in 20 mL. Then, the ammonium acetate was added to obtain a solution of 0.6 M, and the flask was placed on a grill with vigorous agitation at 50 °C. Then, the pH was adjusted to 2 with HNO_3 (DEQ). Once the complete solution of ammonium acetate was assured, 30 mL of gallium acetyl-acetonate solution was added, and the agitation was continued for 24 h. After completion of agitation, the solution was placed in a PARR-brand reactor under thermal treatment at 240 °C for 72 h. Thereafter, the autoclave was cooled until reach room temperature. The synthesized material was recovered, rinsed three times with acetone and dried at 100 °C for 12 h. In order to increase the grade of crystallinity, the material was placed inside a quartz-cell coupled with a tubular oven under a N_2 atmosphere and calcined at different temperatures (400, 600, 800 and 950 °C) for 15 h.

2.2. Physicochemical characterization

The structural properties of the as-prepared materials were analyzed by X-ray diffraction with a Rigaku MiniFelx II-type equipment with Cu Kα radiation (30 kV, 15 mA) at a scan rate of 2 °C min^{-1}. The analyses of the photoelectron spectroscopy obtained with the X-ray study was used to major understand the state of the surface, composition and the electronic structure of GaN using an Intercovamex Equipment XPS 110. The superficial and textural characterization of the fresh material was performed with an Auto-sorb 3B using nitrogen physisorption. The morphology of the synthesized particles was observed by a transmission electron microscope (JEOL, JEM-2010F) and a scanning electron microscope (JEOL 6490LV), which was used to perform a chemical composition analysis (EDS). The photoluminescence (PL) spectroscopy characteristic of GaN was recorded at room temperature and examined at 325 nm using a Xenon lamp with photoluminescence spectroflourometer (Horiba).

2.3. Electrochemical characterization

For electrochemical analysis, three milligrams of GaN prepared with benzene as a solvent and heat-treated at 950 °C GaN, 3 μL of Nafion solution (Aldrich, 5 wt%), 60 μL of ethanol (CTR, 99.95) and 30 μL of water were ultrasonicated for 30 min. 6 μL of this ink were deposited over an ITO film (8–12 Ω/sq, A=0.09 cm^2) and dried for 40 min. Then, a three-electrode standard electrochemical cell was employed. A carbon rod and a Calomel (SCE) electrode were used as counter and reference electrodes, respectively. Solution 0.1 M of KCl was used as supporting electrolyte. Prior to use, the solution was purged with argon for at least 15 min. The *i–E* characteristics were recorded in the interval from 0.0 V to − 1.0 V/SCE using linear sweep voltammetry (LSV) at scan rate of 5 mV/s and presented as Tafel plots (log *i* versus *E*). The electrochemical experiments were done with a Potentiostat/Galvanostat (VersaStat 3).

3. Results and discussions

3.1. XRD analyses

3.1.1. Pressure effect of the solvent

The first stage of this investigation is focused on determining the most appropriate and efficient solvent as well as its effect during preparation of GaN at low temperature using a solvothermal approach as an environmentally friendly route of synthesis. In Fig. 1, the results of the X-ray diffraction patterns employing different solvents are depicted from $2\theta=20$ to 80. According to this, the obtained materials present an amorphous structure. It is interesting to note that such an XRD-patterns display two well-defined wide peaks at $2\theta=36$ and 64, no matter the solvent in turn, corresponding to typical reflections for galium nitrate. Moreover, the detected crystallinity increases with respect to vapor pressure of the