Materials Letters 96 (2013) 34–37

Contents lists available at SciVerse ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Close space vapor transport of gallium nitride in vacuum

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A R T I C L E I N F O

Article history:
Received 28 November 2012
Accepted 3 January 2013
Available online 11 January 2013

Keywords:
Gallium nitride
Close space vapor transport
Solar cells
Photoluminescence

A B S T R A C T

GaN synthesized by close space vapor transport in vacuum using GaN powder as the source material is reported. According to X-ray diffraction measurements, samples grown onto sapphire substrates are polycrystalline with the wurzite structure, while those grown onto fused silica substrates are amorphous. Scanning electron microscope and energy dispersive spectroscopy results show that the surface of the samples is composed of rounded droplets of GaN. Room temperature photoluminescence shows near band-edge emission and a broad defect band. Possible mechanisms allowing the deposition of GaN from the vapors of GaN powder are discussed.

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1. Introduction

GaN and its ternary alloy $In_xGa_{1-x}N$ are very attractive materials for applications in optoelectronic devices as light emitting diodes (LEDs), transistors and lasers [1,2]. Recently, semiconductor nitrides (III-N) and their ternary alloys have been also considered as candidates for the fabrication of thin film and tandem solar cells due to their wide range band gap variation (from 0.64 up to 6.14 eV at 300 K) that covers the whole visible range and a large part of the solar spectrum. Moreover, they have good stability at high temperatures, excellent electrical and thermal conductivity and can be obtained as n or p type semiconductors [3,4]. These features make GaN and related compounds promising materials for production of pin structure (p-GaN/$In_xGa_{1-x}N$/n-GaN) based solar cells [5].

Different methods have been developed to deposit GaN on different substrates. The more conventional ones are molecular beam epitaxy (MBE) and metal–organic chemical vapor deposition (MOCVD) [6–8] both requiring expensive equipment and/or reagents. While it is not a limiting obstacle for light emission devices, in the particular case of solar cells applications, it would be essential to find inexpensive preparation techniques of III-N semiconductors.

In this paper we report the use of close space vapor transport (CSVT) technique to prepare GaN compound in vacuum. Comparing with MBE and MOCVD, CSVT is a low cost preparation procedure which has been extensively used for the fabrication of CdTe/CdS solar cells. However, the use of this technique to grow GaN represents a challenge due to the characteristic thermodynamic and kinetic properties of this compound, quite different from those of CdS or CdTe. As a first issue it can be pointed out that the vapor phase in the equilibrium phase diagram of GaN is largely composed of N_2 molecules, while the vapor pressure of Ga is extremely small even for high temperatures. This means that the sublimation of GaN is not congruent and the composition of the evaporating source can strongly change during the sublimation process, except if the equilibrium N_2 vapor pressure is provided. At temperatures around 1000 °C, at which GaN decomposes [9], the equilibrium vapor pressure of N_2 is extremely high: 2–6 GPa have been reported between 1200 °C and the congruent melting temperature of 2215 °C [10]. A second important issue is that N_2 molecules have a very strong binding energy of around 9 eV/molecule, which makes it impossible to decompose N_2 vapor molecules in the growth chamber by thermal means. In fact, normally other precursors as ammonia or atomic nitrogen from an RF source are used to grow GaN films. For these reasons, the formation of GaN by CSVT without the use of conventional precursors entails the revision of the thermodynamics and kinetics of the decomposition of GaN.

2. Materials and methods

The sublimation system (CSVT) uses a graphite boat located in a heated plate at around 900 °C in vacuum. To reduce the degradation of the GaN powder source as much as possible

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0167-577X/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.matlet.2013.01.011

Fig. 1. Semi-closed graphite boat used for the preparation of GaN by close space vapor transport.

(Aldrich 99.999%) due to the very incongruent sublimation of GaN, a semi-closed graphite crucible was used. As shown in Fig. 1, it has a screw cap (left) that can be threaded onto the lower part containing the GaN source powder and the substrate (right). Growth experiments were performed in vacuum using a pump that provides a base pressure of around 1 Pa. The deposition was carried out on sapphire or fused silica substrates.

For structural characterization, a PANalytical XPert PRO diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å) was employed. Measurements were carried out at 1° grazing incidence from 15° to 80° in steps of 0.03° and a time step of 5000 s. Images of the surface of the samples were taken using a scanning electron microscope (SEM) Jeol JSM-6300 while atomic concentration measurements by energy dispersive spectroscopy (EDS) were obtained with an XFlash detector 5010 from Bruker with an acceleration voltage of 20 kV installed in the microscope. Photoluminescence (PL) spectra were obtained using a He–Cd laser with excitation wavelength of 325 nm and output power of 16 mW, at room temperature. The sample emission was focused into an Acton SpectraPro 2500i Spectrograph and detected by a photomultiplier tube. All the spectra were corrected taking into account the spectral response of the system.

3. Result and discussion

Fig. 2 shows the diffractograms of samples grown on fused silica (A) and sapphire (B) substrates at a temperature of the heated plate of 900 °C for 10 min. In sample B, almost all the peaks can be indexed as corresponding with wurzite GaN (pdf number 897522) with lattice parameters $a = b = 3.189$ and $c = 5.185$ Å. For comparison, a reference diffractogram of GaN is shown. There are two small peaks that do not correspond to GaN at $2\theta = 33°$ and 62°. They presumably can be assigned to any crystalline phase of gallium oxide. Samples grown on fused silica substrate did not show peaks but only wide bands probably due to amorphous material. But in both kinds of substrates, EDS analysis indicates the presence of N and Ga onto the surface of the substrates. The morphology of the sample B is shown in Fig. 3. As can be seen, the surface is covered by small spheres of around 4 μm diameter.

The fact that GaN has been formed from the sublimation of the GaN powder has some implications related with the kinetics of this process. As mentioned earlier, it is impossible to decompose N_2 vapor molecules in the growth chamber by thermal means, because of their very strong binding energy of around 9 eV/molecule.

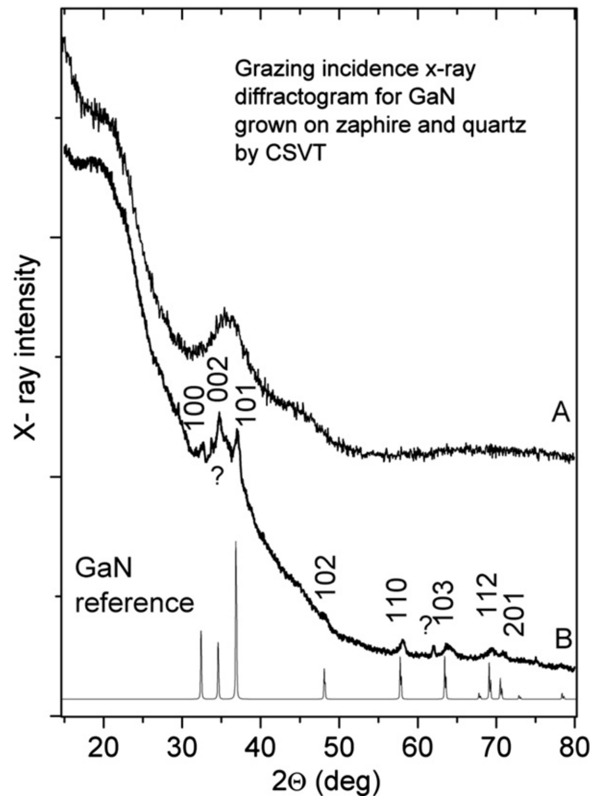


Fig. 2. Diffractograms of samples grown on fused silica (A) and sapphire (B) substrates.

Then, assuming that the decomposition of GaN occurs following the reaction

$$2GaN^{solid} \rightarrow 2Ga^{gas} + N_2 \quad (1)$$

it would be necessary to invoke an alternative mechanism for the dissociation of N_2 to explain the formation of GaN by CSVT.

It has been proposed that liquid Ga can catalyze the N_2 decomposition [11]; this process is controlled also by a kinetic barrier that has been evaluated to be around 3 eV [12]. Then, it could be thought that GaN formation by CSVT proceeds through a sequence of Ga liquid droplets deposition and further Ga nitridation under the high flux of N_2 atoms. The presence of the spheres in the surface seems to support the presence of Ga droplets as precursors of GaN. However, the barrier of 3 eV for Ga catalyzed decomposition of N_2 is still very high and it leads to a Ga catalyzed dissociation probability $e^{-3\ eV/kT}$ (k is the Boltzmann constant and T the absolute temperature) that at 1273 K results in 1.3×10^{-12}. This is a very small number even if the pre-exponential factor, i.e. the N_2 molecules flux impinging the Ga surface, is very high. The vapor pressure P of N_2 in GaN at the same temperature is near 2×10^6 Pa; then the flux of N_2 molecules impinging the Ga surface can be calculated (using the well known expression $P/(2\pi kTm)^{1/2}$) to be $2.8 \times 10^{24}\ cm^{-2}\ s^{-1}$. Taking into account the probability of dissociation calculated above, the flux of dissociated N atoms in the liquid Ga drops would be approximately $7.3 \times 10^{12}\ cm^{-2}\ s^{-1}$. This is a very small flux to be considered as the reason for the formation of GaN. For example, the amount of N atoms in one monolayer of GaN is in the order of $10^{14}\ cm^{-2}$; then with the above calculated flux, 100 s would be necessary to grow only a monolayer of GaN. For this reason, the mechanism of Ga catalysis (at least considering activation energy of 3 eV) should be withdrawn.

Another possible reason for the formation of GaN in CSVT is related with the vapor species produced by GaN during

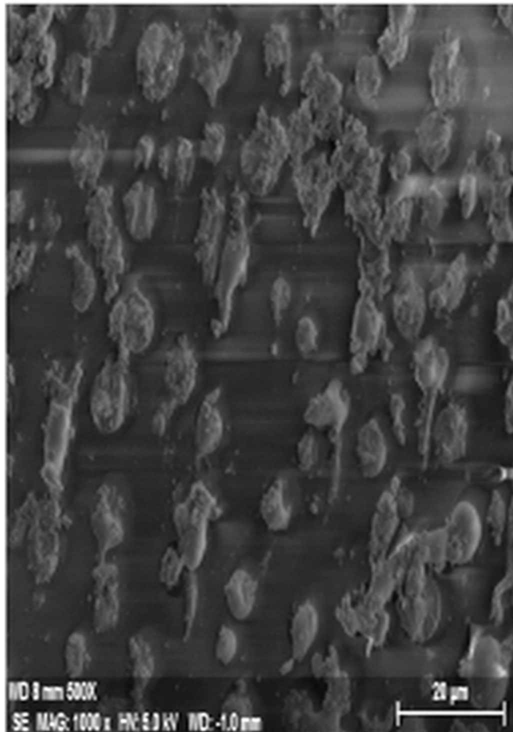


Fig. 3. SEM micrograph of a sapphire substrate surface after the growth of GaN by CSVT.

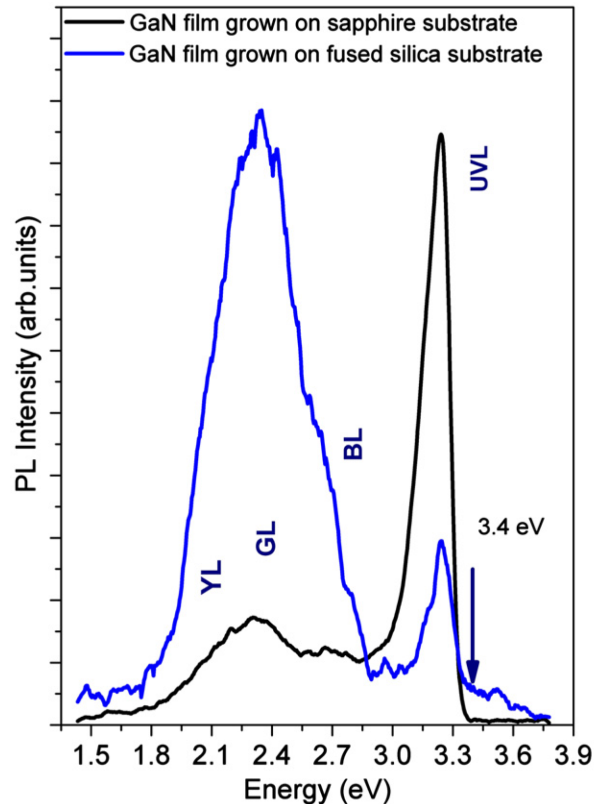
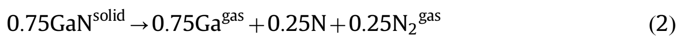


Fig. 4. PL spectra of GaN thin films grown on different substrates.

decomposition. After a comparison of literature data with thermodynamic calculations, a decomposition reaction different from (1) has been suggested [13]:



$$0.75\text{GaN}^{\text{solid}} \rightarrow 0.75\text{Ga}^{\text{gas}} + 0.25\text{N} + 0.25\text{N}_2{}^{\text{gas}} \quad (2)$$

According to this reaction, during GaN decomposition, a part of the nitrogen would evolve as atomic nitrogen. This atomic nitrogen would be unstable and will recombine to form N_2 molecules during collisions in the vapor or with the walls of the container. This hypothesis could explain the deposition of GaN by CSVT. In fact, in this technique, the distance from the source to the substrate is very small; this could help a large fraction of the nitrogen atoms, emerging from the source, to reach the substrate surface. Also in this case, Ga droplets can play a catalytic role.

Room temperature PL spectra of GaN films grown on different substrates are shown in Fig. 4. An intense near-band-gap-edge (NBE) luminescence centered at around 3.25 eV can be remarkably seen in the spectrum of the sample grown on the sapphire substrate. This emission, with reduced intensity, is also observed in the sample grown on the fused silica substrate. In both samples a broad defect band that can be composed of the well known blue, green and yellow luminescence (BL, GL, YL) is observed as well. Normally these bands have been ascribed to the presence of Ga and N vacancies, and oxygen or deep level impurities, as well as amorphous phases [8,14,15]. This is consistent with the non-stoichiometric composition in these GaN thin films, which was confirmed by EDS measurements. The presence of the GL and BL bands could also be explained by the combination of gallium vacancy clusters and oxygen impurities denoted as V_{Ga}–O_N complexes, which are preferably bound to dislocations [16–18]. On the other hand the PL spectrum of the GaN films deposited on fused silica exhibited a stronger green–blue emission peak centered at 2.34 eV.

4. Conclusions

GaN compound was prepared using a CSVT configuration in vacuum by the sublimation of GaN powder. As revealed by XRD, samples grown onto sapphire substrates present the wurzite phase of GaN while the morphology of the substrate surface suggests that the formation of GaN is mediated by liquid Ga. However, only the catalytic effect of liquid gallium in the decomposition of the N_2 molecules does not seem to explain the formation of GaN in these conditions. A previous suggestion of the formation of N atoms during the decomposition of GaN seems to be a more realistic explanation. Intense luminescence in these GaN thin films was enough to be observed with the naked eye in an illuminated room. This paper opens a route to obtain GaN using a simple and not expensive method.

Acknowledgments

The authors acknowledge financial support for this work from CONACYT-SENER under contract 151076 and ICyTDF PICCO 10-29. This work was partially supported by DGAPA-UNAM PAPIIT Projects IN102411 and IB101612, CONACyT México under Project 153948 and ICyTDF Project PICCO 10-73 and UACM Project PI2011-52. OdM and GSCP acknowledge support from CONACyT-México.

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