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Growth on GaN and GaAs on fianite by MOCVD capillary epitaxy technique

A. N. Buzynin[1], V. V. Osiko[1], Yu. N. Buzynin[2] and B. Pushnyi[3]
[1]*General Physics Institute of RAS,*
[2]*Institute for Physics of Microstructure of RAS,*
[3]*Ioffe Physical-Technical Institute,*

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Heteroepitaxial GaN and GaAs films were grown by both conventional two-step MOCVD and the new “capillary epitaxy” technique on (001) and (111) fianite (YSZ) substrates. The capillary epitaxy technique was investigated for the example of GaAs films growth on a YSZ substrate. This technique allows both the reduction of the minimum thickness and the improvement of the quality of III-V films. PL spectra of undoped GaN films on YSZ were studied.

1 Introduction

Fianite (or yttria stabilized zirconia - YSZ) has a number of significant advantages in comparison with other insulating substrate materials, as follows: good insulating properties (10^{12}Om.cm at 300K); and high optical transmission in a wide wavelength range including the visible. Fianite is a good epitaxial partner for $A^{III}B^{V}$ compounds because of their crystallochemical and physical characteristics (table 1).

Epitaxial Si films on YSZ prepared by the pyrolysis of silane in a hydrogen atmosphere [1] and by the chloride vapor phase technique [2] at a temperature of more than 1000°C have been reported. To diminish the negative role of the difference in thermal expansion coefficients between epitaxial pairs it is necessary to lower the epitaxial temperature to about 650°C. We have reported about thin GaAs films on YSZ prepared by the metallorganic chemical vapor deposition (MOCVD) [3]. GaAs films on YSZ substrates have better properties than those on either sapphire or SI-GaAs due to better structural and electrical characteristics, and better thermal and radiation stability.

In this paper we report new results about GaN and GaAs films grown on YSZ substrates by the MOVPE and “capillary epitaxy” [4] technique. The source materials were TMG and AsH_3 for GaAs or NH_3 for GaN_3 films. The films have been characterized by electron microscopy (TEM and SEM), X-ray diffraction (XRD), reflection high-energy electron diffraction (RHEED), luminescence, secondary - ion mass spectroscopy (SIMS) and Van der Pauw measurements.

2 Experiment

2.1 Preparation of the YSZ Substrates

The single YSZ crystals, consisting of ZrO_2 stabilized with 10, 15 and 21 mole per cent of Y_2O_3, were grown by the skull melting technique [5] at 3000°C in air (RF power – 160 kW, frequency – 1.67 MHz). The YSZ crystal block dimensions were large (40-80 mm in cross section and 80-100 mm in length). As-grown YSZ crystals can have both block crystalline and single crystalline structure. We used only single crystalline YSZ with the best structural perfection for wafer preparation. YSZ (100) and (111) oriented wafers were prepared by a multistage technique [6] using ultra dispersed diamond at the mechanical treatment stage.

The chemical composition of the YSZ crystals has been confirmed by x-ray wavelength dispersion analysis using the “Camebax 50SX” SEM. The analysis of impurity compositions of both bulk YSZ crystals and the surface layer of wafers has been performed by x-ray fluorescence spectral analysis using the “VRA-3” instrument. The results of this investigation (Table 2) showed that the mechanical treatment of crystals resulted in the increase of some impurity concentration (Al, Ca, Na, K, Si). The wafers were subjected to additional annealing in order to reduce the concentration of these impurities and to optimize the physical-chemical state of wafer surface before the epitaxy. Recrystalliza-

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tion annealing of YSZ wafers resulted in both removal of impurities and improvement of crystal perfection [7].

2.2 Capillary epitaxy of GaAs on YSZ

The capillary epitaxy technique [4] is based on covering the YSZ wafer with the thin film of A component, and subsequently saturating the film with the corresponding B component until the formation of III-V continuous layer. After that, III-V films were grown to the needed thickness. This technique was studied for the example of GaAs heteroepitaxial growth on YSZ substrates. It was found that the GaAs layers could be grown only within a narrow temperature range of about 550-600°C. When the buffer Ga layer is absent the films have polycrystalline structure and a rough surface. The minimum thickness of these films was about 1,5-2μ. In contrast, thin (50 nm) GaAs films can be obtained after Ga layer formation using the “capillary epitaxy” technique [4].

Figure 1 shows SEM micrographs of GaAs films prepared on YSZ by both conventional MOCVD (Figure 1a) and the capillary epitaxy technique (Figure 1b) at the initial stage of growth, and NH_4J graphoepitaxy on an amorphous Al substrate (Figure 1c,d). An analogy between the helpful action of capillary forces for the new capillary epitaxy technique and for graphoepitaxy was suggested earlier [8]. The formation of layers in both capillary epitaxy and the graphoepitaxy technique take place from creation and coalescence of three-dimensional nuclei. As in the case of graphoepitaxy using surface active substances [8], the use of capillary forces at the first heteroepitaxial stage of the GaAs/YSZ film formation resulted in the following consequences:

1. epitaxial nuclei density increased;
2. the nucleus dimension decreased;
3. the nucleus habit became more flat;
4. the epitaxial orientation of the nuclei improved.

As a result, the minimum GaAs/YSZ film thickness was decreased to 50 nm, and the structural perfection and surface morphology of the films were improved. Single crystalline 50-500 nm thick GaAs(100) films on YSZ(100) were prepared. The submicron GaAs films grown by the capillary epitaxy technique had high resistance. For n-type GaAs films, SiH_4 was used as dopant source. Electron concentration in the films was in the range of $5 \cdot 10^{16}$ to $5 \cdot 10^{17}$ cm^{-3}. SIMS data showed that background impurity concentration was similar to that in GaAs/GaAs films. The layer -by-layer SIMS analysis indicated a uniform distribution of impurities in the GaAs films and a sharp distribution of Zr, O and Y across the film-substrate interface.

According to figure 1, better wetting of substrate led to better film structure both for graphoepitaxy of NH_4 on amorphous Al and capillary epitaxy of GaAs on YSZ.

2.3 GaN Films on YSZ

GaN films on YSZ substrates were grown both by conventional MOVPE [9] and by the “capillary epitaxy” [5] technique similarly to the GaAs films. The thin (~50nm) Ga layer on the YSZ substrate was pre-deposited by the MOD technique before the GaN MOVPE growth in TMG-NH_3-H_2 system at 1025°C in the case of the “capillary epitaxy” technique. The GaN films had a mosaic structure. The film-substrate orientation relationships are GaN(0001)/YSZ(100) and GaN(0001)/YSZ(111). Typical examples of PL spectra of undoped n-GaN films are shown in Figure 2.

The work on improvement of the structural perfection of GaN films on YSZ substrates is in progress.

3 Summary

GaN and GaAs films were grown by conventional MOCVD and by a new capillary epitaxy technique on YSZ substrates We have studied the capillary epitaxy growth of GaAs films on YSZ substrates in detail. There is an analogy between the helpful action of capillary forces in capillary epitaxy technique and graphoepitaxy using surface-active substances. Use of capillary forces allows both the reduction of the minimum thickness and the improvement of III-V film quality. The growth condition for GaAs submicron single crystalline films with high structural perfection have been established. The grown GaN films had mosaic structure. The film-substrate orientation relationships were GaN(0001)-YSZ(001), GaN(0001)-YSZ(111) and GaAs(001)-YSZ(001). The luminescence spectra of undoped n-GaN films on YSZ substrates were obtained.

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FIGURES

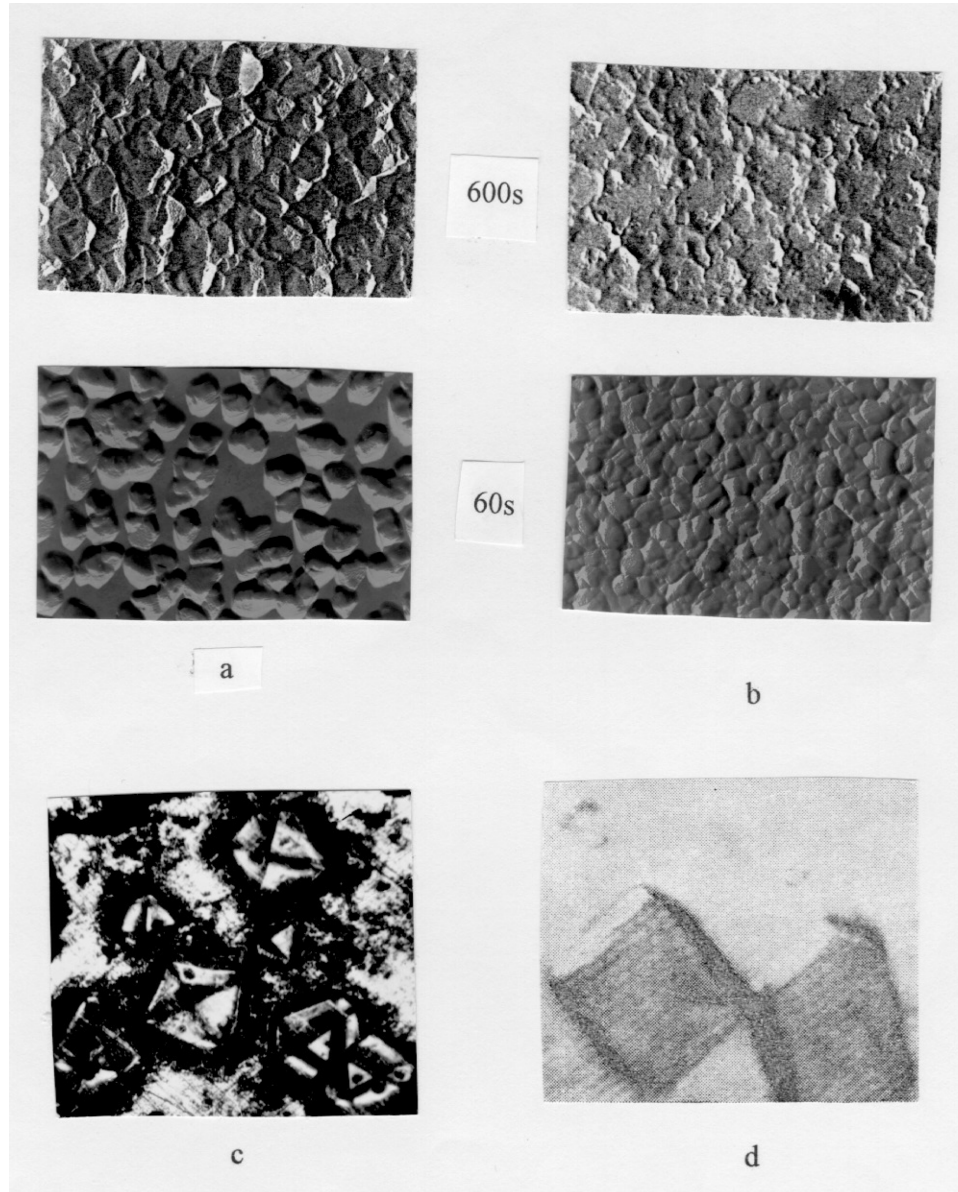

Figure 1. SEM micrographs of GaAs films prepared using both conventional MOCVD (a) and capillary epitaxy MOCVD(b) at the initial stage of epitaxy on YSZ substrates (60 and 600s after procedure beginning, 20000x) and optical micrographs of NH_4J flat crystals prepared by the graphoepitaxy technique on amorphous Al substrates without (c) and with(d) a surface active substance (100x).

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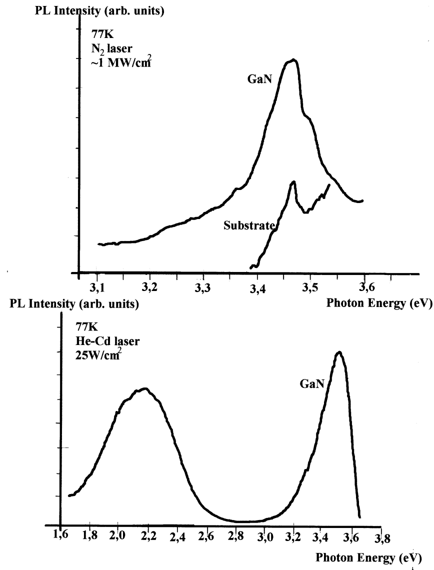

Figure 2. Luminescence spectra of undoped GaN films on a YSZ substrate.

TABLES

Table I. Some characteristics of YSZ and $A^{III}B^{V}$ crystals.

Crystal	Lattice		T_m,°C (melting point)	Therm. Exp. Coeff. 10^{-6} deg^{-1}	E_g, eV
	Type	a, Å			
YSZ $(ZrO_2)_{100-x} \cdot (Y_2O_3)_x$	Cubic (fluorite)	5,141(x=10) 5,157(x=15) 5,198(x=21)	2800	11,4 (15-1000°C)	
GaAs	Cub(sf)	5,65	1283	5,4	1,43
GaP	Cub(sf)	5, 445	1467	4,7	2,26
GaN	H(v)	a=3,186 c=5,178	1700	5,6 7,8	3,4

Table II. Impurity concentration in YSZ single crystals, YSZ-wafers and GaAs/YSZ films

Element	YSZ crystal, wt%	YSZ wafer, wt%	GaAs/YSZ, at. cm^{-3}
Al	0.0004	0.001	$5x10^{17}$
Ca	0.001	0.003	$5x10^{17}$
Mg	0.0005	0.0005	
Na	0.0001	0.003	$2x10^{17}$
K	0.0005	0.001	$5x10^{16}$
Si	0.001	0,015	$1x10^{17}$
Cu	0.0005	0.0005	
Fe	0.0004	0.0004	$5x10^{16}$
Mn	0.0001	0.001	

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