Vacuum xxx (2016) 1–6

Contents lists available at ScienceDirect

Vacuum

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

Reinforcement role of GaP nanowires in a ZnO layer prepared by RF sputtering☆

Jozef Novák [a, *], Agáta Laurenčíková [a], Stanislav Hasenohrl [a], Ivan Novotný [b], Jaroslav Kováč [b], Marian Valentin [c], Jaroslav Kováč Jr. [b]

[a] Institute of Electrical Engineering SAS, Dubravska 9, 841 04 Bratislava, Slovakia
[b] Slovak University of Technology, Institute of Microelectronics and Photonics, 812 19 Bratislava, Slovakia
[c] Polymer Institute SAS, Dubravska 9, 845 41 Bratislava, Slovakia

ARTICLE INFO

Article history:
Received 15 July 2016
Received in revised form
11 October 2016
Accepted 8 November 2016
Available online xxx

Keywords:
Nanowire
Compound semiconductor
Nanoindentor
Hardness

ABSTRACT

This paper presents a thin nanocrystalline ZnO layer with embedded GaP nanowires (NWs). The NWs were grown in vapour-liquid-solid (VLS) mode by metal organic vapour phase epitaxy (MOVPE) at Au seeds formed from a very thin Au layer. The NWs were finally embedded in ZnO using deposition by RF sputtering combined with etching steps that resulted in a compact antireflection layer. We studied properties of such compact NWs structure by means of x-ray diffraction and atomic force microscopy. The study of mechanical properties was performed by nanoindentation measurements. The nanoindentation measurement showed that the incorporation of GaP nanowires into a ZnO layer led to increased hardness compared with that of a pure ZnO layer. The compact GaP NW/ZnO layer structure also exhibited some degree of pseudoelasticity. In addition, the mechanical properties of the compact nanowire layer are sufficiently robust to allow the thermo-compression bonding on the top of the structure.

1. Introduction

Recent advances in nanotechnology have enabled the well-controlled bottom-up fabrication of nanowires (NWs) and their controlled lateral assembly using pre-patterning by electron beam lithography [1] or nanoimprint lithography [2,3]. Another very successful method for assembling NWs is the deposition of ultra-thin metallic layers that are subsequently annealed, which leads to the formation of nanoseeds [4,5]. The versatility of NWs makes them very interesting for making various heterostructures in the form of core-shell structures [6]. Mechanical properties of NWs, their internal phase changes [7], incorporated strain [8] and other related properties are widely studied [9]. Surfaces of NWs can be functionalized and, because of a very high surface-to-volume ratio, they are ideal building blocks for various sensors, anti-reflection coatings and objects that can interface inorganic and organic materials. In addition, the formation of core-shell structures is an effective method of passivation of surface states of core NWs. Gallium phosphide NWs belong to widely studied structures as they can lead to many possible applications. Previous studies presented the preparation of GaP NW anti-reflection coatings [10], catalysts for the splitting of CO_2 molecules for useful chemicals [11] and as holders for the immobilization of DNA molecules [12].

However, nanowires are fragile. They can break under tiny mechanical stresses. This is a major problem as anti-reflection is worse at damaged NW assemblies. But a NW assembly can be fortified by filling gaps between NWs with some other optical material. The realization of core-shell structured NWs is avery effective strategy to eliminate the fragility of NWs. The core-shell structure can provide a permanent protection of core NWs against the impact of exterior forces. The added material should fill up the space between the NW cores. This will result in a compact layer with embedded NWs that will combine mechanical and optical properties of both materials. With the progress of growth or deposition technology of nanomaterials, a large number of III–V core-shell NWs have been realized, including core-shell nanowires based on InAs/GaAs [13], InAs/InP [14], GaP/ZnO [15], ZnO/ZnSe [16] and GaAs/GaP [17].

☆ The paper was presented at the JVC 16 conference in Portoroz.

* Corresponding author.
E-mail address: eleknova@savba.sk (J. Novák).

http://dx.doi.org/10.1016/j.vacuum.2016.11.014
0042-207X/

In this paper, we report on the incorporation of GaP nanowires into a ZnO layer by a combination of RF sputtering and MOVPE growth. We investigated the formation of a compact GaP/ZnO core/shell nanostructured layer where GaP nanowires play a supporting and reinforcement role. Our previous results showed that ZnO is deposited in the form of nanograins arranged into nanocolumns with a longitudinal shape [6,18]. The nanocolumns are perpendicularly oriented to the surface of GaP NW cores. ZnO nanocolumns can form into a compact ZnO layer if ZnO is deposited for a sufficiently long time. ZnO nanograins fill spaces between the NWs, and the resulting structure is compact and very hard [19]. We investigated mechanical properties of such a nanostructured GaP NW/ZnO system using nanoindentation measurement.

2. Experimental

GaP NWs were grown on GaP <111)B oriented substrate by MOVPE using VLS mode (vapour-liquid-solid). It is a NW growth mechanism from vapour phase during which an alloy phase catalyzes and rapidly adsorbs a source material vapour to a supersaturation level which subsequently initiates crystal nucleation at the liquid–solid interface [18,20]. GaP nucleated into the NWs at Au seed particles, which coalesced from a sub-nanometre thick Au layer deposited on the substrate by evaporation.

Upon the deposition of the Au layer, the substrate was heated under a gradually increasing phosphine (PH_3) flow in an AIX 200 low-pressure MOVPE reactor. Once temperature $T_a = 650$ °C was reached, it was annealed during 10 min under a PH_3 flow. This led to the formation of Au seeds with 20–40 nm in diameter and a density of 400 seeds per 1 square micrometre. GaP NW growth was subsequently performed at a temperature of 500 °C and pressure of 100 mbar. The typical as-grown GaP NWs were ~0.5 μm long. They were slightly conical. Their mean diameter was 80 nm at the base and 25 nm under the Au particle.

The NWs were subsequently covered with a thin nanocrystalline Ga-doped ZnO layer by sputtering in a Perkin Elmer planar RF diode system, using a ceramic ZnO:Ga_2O_3 (98 wt%:2 wt%) target 100 mm in diameter. The sputtering chamber was evacuated to a base pressure of 10^{-5} Pa before the admission of an Ar working gas (99.999% purity). ZnO was deposited on the substrate at room temperature at an Ar pressure of 1.3 Pa and sputtering power at 600 W. Thin ZnO:Ga layers were deposited at a constant rate of ~30 nm/min. The RF-sputtering conditions were adjusted to deposit very uniform ZnO layers with the aim to form core-shell GaP/ZnO NWs and then to extend the shell thickness so that the shells of neighbouring NWs would merge [19].

X-ray diffraction measurement (XRD) proceeded in a high-temperature HTK 1200 N chamber that was part of a Panalytical X'Pert Proautomatic powder diffractometer. The instrument used a copper X-ray tube ($\lambda_{K\alpha} = 0.15406$ nm) and an ultra-fast semiconductor detector PIXcel.

Nanoindentation tests were carried out with a Hysitron Tl-750 nanomechanical test instrument from Hysitron Inc. The indentation system used an atomic force microscope (AFM) as a platform, and a load–displacement transducer. Samples of the structure were pressed with an indentor tip of diamond Berkovich type. A comprehensive indentation procedure was applied at a precisely controlled force and displacement of the indentor. During the indentation procedure, the force was increased to a maximum value (loading) and then decreased to zero (unloading). Loads between 100 and 1000 μN were applied. A small shift between the loading and unloading curves was caused by a short (2 s) constant loading at a maximal loading force before unloading. The load–displacement curves were used for the calculation of the hardness and Young's modulus of elasticity of tested structures.

The size, shape and structure of the core-shell GaP/ZnO NWs were studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

3. Results and discussion

Representative topographic images (AFM contact mode) of a ZnO layer deposited on GaP substrate and a GaP/ZnO layer with embedded GaP NWs are shown in Fig. 1a and b. Our previous TEM and SEM study showed that such ZnO layer consists of nanograins. The size of the crystallites lies between 10 and 40 nm with an average of 27 nm [6]. The surface morphology of a 250 nm thick planar ZnO layer is shown in Fig. 1a. The surface structure probed by AFM responded to its internal grain structure, and the root-mean-square (rms) estimated from an area of 5×5 μm^2 was 3.3 nm.

Deposition of ZnO nanograins on the GaP NWs is more complicated. At first, the ZnO nanograins are arranged into nanocolumns that are normally oriented to the NW sidewalls. Each GaP facet of the NW is a base for several ZnO nanocolumns. The whole shell consists of many nanocolumns formed around about the GaP core (see Fig. 2). In addition, detailed SEM study showed that ZnO nanograins, streaming from the source towards the NWs, had a tendency to change their slightly conic shape. This gradually led to GaP/ZnO NWs with a cylindrical shape rather than a conic one. With further ZnO deposition, top sections of GaP/ZnO NWs grew wider than their lower sections. This reduced and finally prevented ZnO deposition at the foot of the NWs where voids were formed. To circumvent this problem and form a compact ZnO shell layer without voids, we alternated ZnO deposition with ZnO etching by Ar ions. This technique needed to be carefully optimised, but in the end it allowed us to prepare a compact ZnO layer that completely engulfed the NWs (see Fig. 1b). Its detailed description is presented elsewhere [19]. The total thickness of such a compact ZnO layer with embedded GaP NWs was approximately 500–600 nm. The layer fully covered top parts of all GaP NWs. The layer that accumulated on NW tops was very thin (20–50 nm). Consequently, the surface morphology of the compact layer followed differences in NW lengths. Fig. 1b presents an AFM surface topography scanned on an area of 5×5 μm^{2}with a root-mean square (rms) of 10.42 nm.

Properties of the crystalline structure were observed by XRD analysis. Fig. 3 shows a typical X-ray diffraction pattern of sputtered ZnO deposited on the GaP substrate and as a shell layer on GaP NWs. The diffraction peaks were identified as belonging to both ZnO and GaP. The pattern associated with the sputtered shell layer on the NWs is quite similar to that of bulk ZnO, and it reveals a hexagonal wurtzite structure but the intensity of signal from the NWs was significantly lower (15x). The (002) line of all sputtered films shifted left toward the reference ZnO (002) line (2 theta = 34.42°). The (002) line shift to the left most likely occurred because of a porous crystalline structure. If the simultaneously diffracting volumes of relaxed and constrained materials in the part of the film probed were unequal, an asymmetric line profile broadening can be expected. This asymmetry may be caused by compositional variations or by lattice stress gradients in the depth of the analyzed material.

Mechanical properties of the ZnO layers and GaP NW/ZnO structures were studied by nanoindentation measurement. Fig. 4 shows an example of indentation marks taken on the surface a ZnO sample. A set of indentation data was taken from each sample. Fig. 5 compares a set of representative nanoindentation load-displacement curves for a ZnO layer and the compact GaP NW/ZnO layer structure. Both samples were measured under a load of 100, 200 and 1000 μN. To prevent the influence of GaP substrate on the measurement, the maximum penetration depth was limited to

Please cite this article in press as: J. Novák, et al., Reinforcement role of GaP nanowires in a ZnO layer prepared by RF sputtering, Vacuum (2016), http://dx.doi.org/10.1016/j.vacuum.2016.11.014