Thin Solid Films 649 (2018) 232–236

Contents lists available at ScienceDirect

Thin Solid Films

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

Molecular beam epitaxy growth of GaN films on a tungsten carbide/Si template

Sungmin Cho[a], Sungkuk Choi[b], Youngji Cho[b], Sangtae Lee[c], Moonjin Lee[a,d], Jiho Chang[a,b,*]

[a] Department of Convergence Study on the Ocean Science and Technology, Korea Maritime and Ocean University, Busan 49112, Republic of Korea
[b] Major of Electronic Material, Korea Maritime and Ocean University, Busan 49112, Republic of Korea
[c] Department of Offshore Plant Management, Korea Maritime and Ocean University, Busan 49112, Republic of Korea
[d] Korea Maritime Safety Research Divisions, Korea Research Institute of Ships and Ocean Engineering, KIOST, 34103 Daejeon, Republic of Korea

ARTICLE INFO

Keywords:
Gas-source molecular beam epitaxy
Gallium nitride
Silicon
Tungsten carbide
Buffer layer

ABSTRACT

This study examined the growth of GaN layers by molecular beam epitaxy (MBE) using a tungsten carbide (WC) buffer sputtered on a Si(111) surface. The chemical stability of the WC layer against the Ga-Si interaction was verified experimentally. A low-temperature (LT) buffer is essential for the growth of single-crystal-quality, high-temperature gallium nitride (HT-GaN) on a WC surface. In addition, dislocation termination techniques, such as interface formation and the annealing of the buffer layer, were adopted to improve the crystalline quality. The HT-GaN sample grown on the annealed double-buffer-layer (AlN/GaN) revealed an X-ray diffraction full-width at half maximum, Hall carrier density, and carrier mobility of 2260 arcsecs, 4.39×10^{18} cm^3, and 19.4 cm^2/Vs, respectively. The crystalline quality of the GaN layer is discussed in comparison with previously reported GaN/sapphire samples.

1. Introduction

Si substrates for GaN growth offers irreplaceable advantages, such as low cost, high crystal and surface quality, large-area-wafer availability, high thermal stability, and conductivity [1,2]. On the other hand, the large lattice mismatch > 17% between GaN and Si, and the formation of various interfacial layers hinders the growth of high quality GaN film, and the growth of GaN directly on a Si substrate resulted in poor crystal films [3]. A range of growth techniques using various buffer layers (AlN [4], ZrB_2 [5,6], HfN [7,8], and SiC [9,10]), multiple-buffer-layers [11,12], mask-layers (SiN_x) [13,14], and miscut substrates (off-cut Si [15,16]) have been studied. Those growth technologies form the basis of current GaN-on-Si technology. Owing to the efforts of those researchers, the GaN industry has started to take advantage of low-cost substrates. In terms of the cost-performance criteria for light emitting devices (LEDs) [17–19] and power electronics applications [20], both insulating and conducting buffer layers are essential. Among the various buffer layers mentioned above, however, the HfN buffer layer [7,8] is the only conducting buffer for GaN-on-Si technology; hence, more studies on the buffer layer for GaN-on-Si technology is necessary.

In the present study, a tungsten carbide (WC) buffer layer was introduced for GaN growth on a Si substrate [21]. The crystal structure of WC is either α-WC (structure: hexagonal, lattice constant: a = 2.91 Å, c = 2.84 Å) or β-WC (structure: cubic, lattice constant: 4.16 Å). In addition, the structure and lattice parameter of tungsten carbide changes according to the W/C ratio [22]. Therefore, WC is considered a good candidate as a buffer between silicon and GaN.

WC is conventionally known as a surface protection layer for various mechanical tools because of its superior mechanical and chemical robustness [23–25]. On the other hand, it has not been assessed as a buffer layer for nitrides. Therefore, it is important to determine the growth condition of tungsten carbide on a silicon substrate and assess the ability of the layer for successive nitride growth on it.

2. Experimental

WC buffer layers were sputtered on Si (111) substrates by DC magnetron sputtering. To prevent peeling of the WC film, a HF-dipping process was introduced after the organic cleaning of the Si substrates. A 5 N–purity WC target with a 3-in. diameter was used for sputtering. The background chamber pressure was $\sim 10^{-10}$ Torr. A Si-substrate with a 2-inch diameter was introduced into the sputter chamber through a load-lock chamber. The sputtering conditions were optimized. The plasma power, Ar gas flow, and growth temperature were 50 W, 10 sccm, and room temperature, respectively. In this experiment, the

* Corresponding author.
E-mail address: jiho_chang@kmou.ac.kr (J. Chang).

https://doi.org/10.1016/j.tsf.2018.01.057
Received 13 July 2017; Received in revised form 25 January 2018; Accepted 28 January 2018
Available online 31 January 2018
0040-6090/

surface energy (γ = 82.46 mJ/cm^2) of the WC layer was found to be similar to that of the sapphire substrate (γ = 82.71 mJ/cm^2). Therefore, the WC template was considered to be available for the growth of a single crystalline GaN layer [21].

The surface of the WC/Si template was cleaned with the organic solvents (acetone and methanol) and rinsed in DI water for MBE growth. The GaN layers were grown using a gas source molecular beam epitaxy (GS-MBE) system [26]. Metallic Ga was evaporated using a Knudsen effusion cell (K-cell) and NH_3 gas was introduced to the substrate surface through a nozzle. The growth temperature was measured using a thermo-couple placed just behind the sample holder. The thermocouple temperature was calibrated to approximately the melting point of aluminum (~660 °C). After loading the WC-template into the MBE chamber, the substrate was cleaned thermally at 950 °C for 10 min. In this experiment, low-temperature (LT) layers were grown at 630 °C, and high- temperature (HT) layers were grown at 920 °C. The growth rate of the GaN films was altered by the variation in the V/III ratio even under the NH_3-rich growth conditions because of the formation of a transition layer on the growth front [26].

Various samples were prepared to verify the feasibility of the WC buffer layer. First, the necessity of a low-temperature buffer was confirmed. Two samples, (a) HT-GaN/WC/Si-substrate and (b) HT-GaN/LT-GaN/WC/Si-substrate, were compared.

The effectiveness of the well-known dislocation reduction approaches was then verified. Three samples were prepared: (a) HT-GaN/LT-GaN/WC/Si-substrate, (b) HT-GaN/LT-AlN/LT-GaN/WC/Si-substrate, and (c) HT-GaN/annealing/LT-AlN/LT-GaN/WC/Si-substrate.

The surface morphology was analyzed by field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM). X-ray diffraction (XRD) was performed to confirm the crystal quality. The film resistivity was evaluated using a 4-probe. The Hall effect was measured to evaluate the carrier concentration in the Van der Pauw configuration. To characterize the optical properties, photoluminescence (PL) spectroscopy was performed using the 325 nm line of a He-Cd laser in a cryostat cold-finger.

3. Result and discussion

Fig. 1 presents the SEM images and contact angle measurement results. Fig. 1(a) shows a SEM image of the WC/Si-substrate (WC-template); a smooth and mirror like surface was obtained. Fig. 1(b) shows the contact angle measurements. The surface energy (γ) of WC was calculated to be 825 erg/cm^2, which is very close to that of the Al_2O_3 (0001) surface (889 erg/cm^2) [27]. Hence, we considered that the WC buffer could be used as a template for GaN growth.

WC is a robust chemical compound. In its most basic form, tungsten carbide is a fine gray powder, but it can be pressed and formed into shapes for use in industrial machinery, cutting tools, abrasives, armor-piercing rounds, other tools and instruments, and jewelry. WC is approximately two times stiffer than steel, with a Young's modulus of approximately 530–700 GPa [28,29]. This is comparable to the corundum α-Al_2O_3 in hardness and can only be polished and finished with abrasives of superior hardness, such as cubic boron nitride and diamond powder. The electrical resistivity of WC is $2 \times 10^{-7}\,\Omega$ m, which is comparable to that of some metals (e.g. vanadium $2 \times 10^{-7}\,\Omega$ m) [30,31]. The resistivity and sheet resistance of the WC-template was measured to be $1.44 \times 10^{-6}\,\Omega$ m and 9.34 Ω/sq., respectively.

The chemical robustness of the WC film was tested before the GaN layer was deposited. Ga was deposited on the Si(111) and WC/Si(111) surface, simultaneously. Deposition was performed in a thermal evaporator, and a thermal treatment was performed in a horizontal furnace at 1100 °C under a N_2 flow. The horizontal furnace was evacuated during the temperature rising, and 6 N purity nitrogen (N_2) gas was then flowed into the furnace at a flow rate of 1 *l*/min. The thermal treatment was maintained for 1.5 h at 1100 °C. After the thermal treatment, the specimens were removed from the furnace and their cross-sections were observed. Fig. 1(c) and (d) presents cross-section images of the (c) Ga/Si(111) and (c) Ga/WC/Si(111) samples. Many images were taken to confirm the reliability of the result; hence, those figures could be regarded as representative. Unlike Fig. 1(c), there was no evidence of a Ga-Si interaction from Fig. 1(d).

To grow the GaN layers, the WC template surface was cleaned briefly by organic solvents (acetone, and methanol) and cleaned thermally in an ultra-high vacuum chamber at 950 °C for 10 min. The growth was started with the simultaneous supply of Ga and ammonia.

An attempt was made to grow GaN layers with and without a low-temperature GaN buffer (630 °C). Fig. 2(A) and 2(B) show the surface of HT-GaN/LT-GaN/WC layer (sample-(a)) and HT-GaN grown directly on

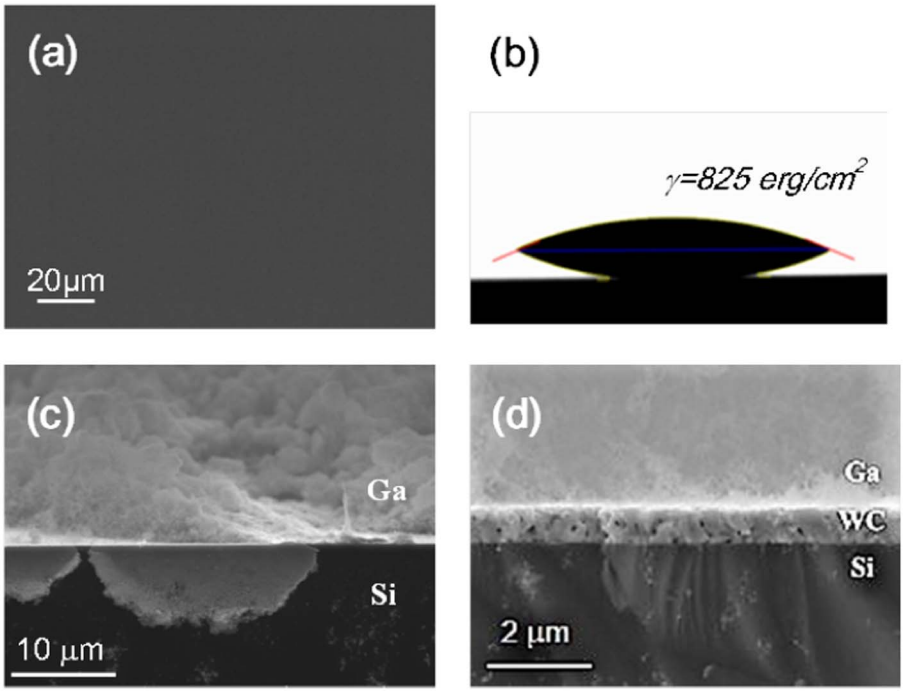

Fig. 1. (a) FE-SEM image of the WC/Si(111) surface, and (b) contact angle measurements of the surface energy. Cross-section images of (c) Ga/Si(111) and (d) Ga/WC/Si(111) samples. Evidence of a Ga-Si reaction was observed from Fig. 1(c).