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Synthesis of homogeneous and high-quality GaN films on Cu(111) substrates by pulsed laser deposition

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Abstract: GaN films have been grown on Cu (111) substrates through growing AlN buffer layer with an in-plane alignment of GaN[11-20]//AlN[11-20]//Cu[1-10] by pulsed laser deposition. It is found that by optimizing the laser rastering program and the epitaxial growth temperature, the thickness homogeneities, surface morphologies and structural properties of GaN films can be greatly improved. Especially, the as-grown GaN films grown at 750 ºC with the optimized laser rastering program exhibit excellent thickness uniformity with a root-mean-square (RMS) thickness inhomogeneity less than 2.8%, and very smooth and flat surface with a surface RMS roughness of 2.3 nm. The as-grown ~102-nm-thick GaN films are almost fully relaxed only with an in-plane compressive strain of ~0.53%. There is no interfacial layer existing between AlN buffer layer and GaN film. Furthermore, as the increase in growth temperature from 550 to 750 ºC, the surface morphologies and structural properties for as-grown ~102-nm-thick GaN films are improved significantly. The achievement of homogeneous and high-quality GaN films brings up a broad prospect for the future application of GaN-based devices on Cu substrates.

Keywords: GaN films; Cu (111) substrates; thickness uniformity; fully relaxed; interfacial layer.

1. Introduction

Gallium nitride (GaN) and its related III-nitrides have acctracted widespread attention due to their excellent optcial and electronic properties. These properties make them possible for the application of light-emmiting diodes, laser diodes, high electron mobility transistors, *etc*.[1-3] So far, GaN-based optoelectronic devices prepared on sapphire substrates have been commercialized. However, due to the poor thermal conductiveity of sapphire, it is poor at heat dissipation and is hard to meet the requirement of high-power GaN-based optoelectronic devices.[4-9]

GaN-based optoelectronic device prepared on high thermal conductivity substrate is an effective approach to solve this problem.[10-12] A Cu substrate is one of the most promising substrates for this purpose because of its high thermal conductivity (395 W/(m·K), 100 ºC).[13] Several groups have already demonstrated that devices prepared on the high thermal conductivity substrates can improve the performance due to the enhancement in heat dissipation.[14-16] They prefabricate the device layers on sapphire substrates, separate the device layers from the sapphire substrates by the laser lift-off techniques, and eventually transfer the device layers on the metals, for example Cu, by the bonding techniques.[14-16] However, this fabrication process is very complex and difficult. On the one hand, this process would increase the cost in the fabrication of devices.[14-15] On the other hand, the soldering involved in this process may decrease the heat dissipation of devices.[14-16] Therefore, epitaxial growth of the GaN-based layers on the metal substrates may be a way to overcome these difficulties. However, it is difficult to use conventional metal-organic chemical vapor deposition and molecular beam epitaxy to grow III-nitrides on thermally active substrates, for example Cu, because these two epitaxial growth techniques usually deploy high growth temperature that may cause serious interfacial reactions between the films and substrates during the initial growth and eventually result in the poor-quality of III-nitrides.[17-18] In this regard, a low epitaxial growth temperature is of paramount importance in epitaxial growth of high-quality III-nitrides on Cu substrates.

Recently, pulsed laser deposition (PLD) technique makes it possible for the epitaxial growth of III-nitrides on thermally active substrates at low temperature.[2-4] The highly energetic pulsed laser ablates the target to ensure the highly kinetic energy of precursors when arriving at substrates. This would effectively suppress the interfacial reactions between the epitaxial layers and the substrates, and make the epitaxial growth of nitrides at a relatively low growth temperature possible.[19-21] So far, many III-nitride films have been grown on metal substrates by traditional PLD,[2-4, 22-24] and the combination of electron cyclotron resonance plasma enhanced metal-organic chemical vapor deposition (ECR-PEMOCVD) and radio-frequency magnetron sputtering.[25-28] Particularly, GaN films grown on Cu substrates by traditional PLD technology have been demonstrated by S. Inoue *et al*.[4] However, GaN films grown by these techniques usually show relatively poor thickness homogeneity due to the highly directional distribution of the precursors on the metal substrates.[2-4, 22-28] If the GaN-based optoelectronic devices are prepared with these GaN films, product qualification rate would be very low.[19] What is more, GaN films grown on Cu substrates lack comprehensive study. S. Inoue *et al*. only study the properties of as-grown GaN films on Cu substrates by *in-situ* reflection high energy electron diffraction (RHEED), electron backscattering diffraction, X-ray photoelectron spectroscopy, spectroscopic ellipsometry. These results are not enough for the researchers to understand the properties of GaN films grown on Cu substrates comprehensively.

In this work, we report on the growth of homogeneous and high-quality GaN films on Cu (111) substrates with AlN buffer layer by PLD with optimized laser rastering technology. On the one hand, the application of laser rastering technique integrated in PLD can achieve homogeneous thickness films on the whole substrates.[16, 29-30] On the other hand, we systematically study the surface morphologies, crystalline qualities, and interfacial properties of as-grown GaN films by white-light interferometry, *in-situ* RHEED, scanning electron microscopy (SEM), atomic force microscopy (AFM), polarized light microscopy, high-resolution X-ray diffraction (HRXRD), and high-resolution transmission electron microscopy (HRTEM). This will be beneficial to the researchers who want to understand the growth of GaN films on Cu substrates comprehensively.

2. Experimental

The as-received 1×1 cm^2 Cu (111) substrates were degassed in the ultra-high vacuum (UHV) load-lock chamber with the background pressure of 1.0×10^{-8} Torr at 200 ºC for 10 min, and then were transferred into the UHV-PLD growth chamber with the background pressure of 3.0×10^{-10} Torr. Subsequently, a 60 min annealing process was conducted at 620 ºC to remove residual surface contaminations and achieve atomically flat Cu (111) substrates for the deposition of thin films. Afterwards, the homogeneous AlN films were grown with optimized laser rastering technique reported by W. Wang, *et al* with the nitrogen pressure of 8.0×10^{-3} Torr to achieve abrupt AlN/Cu hetero-interfaces.[31] After epitaxial growth of homogeneous AlN, the distance between the target and substrate was set at 5 cm and the growth temperature of substrate was changed from 550 to 750 ºC with the heating rate of 5 ºC/min to grow GaN films for 30-120 min. During the GaN growth, high purity N_2 with the pressure of 1.0×10^{-2} Torr was supplied through the inert gas purifier and the radio-frequency plasma radical generator operated at 500 W. The energy density of laser was set at 3.0 J/cm^2 with the pulse repetition rate of 30 Hz. Meanwhile, laser rastering was applied to ensure the laser beam scanning on the 2-inch-diamter Ga target with a programmable procedure where scanning rate, step length, starting and ending points were optimized.[19, 31] During the epitaxial growth, the *in-situ* RHEED was applied to monitor the growth condition during the whole course. After epitaxial growth of GaN films, the substrates were cooled down with the rate of 3 ºC/min from growth temperature to room temperature in order to avoid the formation of cracks. The as-grown GaN films were evaluated by white-light interferometry (Y-Wafer GS4-GaN-R-405), *in-situ* RHEED, SEM (Nova Nano SEM 430 Holland), AFM (MFP-3D-S Asylum American), polarized light microscopy (OLYMPUS, BX51M), HRXRD (Bruker D8 X-ray diffractometer with Cu Kα1 X-ray source λ=1.5406 Å), and HRTEM (JEM-2010HR).

3. Results and discussion

The homogeneous AlN buffer layer is grown with the optimized laser ratering program.[19, 31] Subsequently, the GaN thin films are grown on the homogeneous buffer layer AlN films by PLD. Table 1 shows the three different samples with different laser rastering programs. Sample A is the GaN films grown without the utilization of laser rastering program. Sample B is the GaN films grown with identical laser rastering rate of 100 steps/s for each segment along AlN target radius. As for Sample C, the GaN films are grown with the optimized laser rastering program. In this case, the laser rate is 100 steps/s in the target center (S1), and is gradually decreased to 60 steps/s (S2), till 20 steps/s in the target edge (S3).[19]

After epitaxial growth, the thickness distribution of as-grown GaN films is characterized by white-light interferometry. Fig. 1a is a schematic image of as-grown GaN films on Cu substrates at 750 ºC for 60 min. We use the thickness of the 5 points (I-V), as shown in Fig. 1a, to evaluate the thickness distribution of the as-grown GaN films on Cu substrates with ~950-nm-thick AlN buffer layer. Fig. 1b is the thickness distribution of these 5 points, where the thickness inhomogeneity is calculated by the formula in the references.[31-33] From Fig. 1b, we can clearly identify that the RMS thickness inhomogeneity for Sample A is as large as 11.9 %. The thickness of GaN films in the substrate center is as high as 115 nm and then is gradually decreased with the areas away from the substrate center, till 84 nm in the substrate edge. The application of an identical rastering rate over the whole 1×1 cm^2 can reduce the RMS thickness inhomogeneity to 5.6%, as shown in Sample B. This is still not good enough. If an optimized laser rastering program as described above is applied in Sample C, the as-grown GaN film shows a very uniform thickness of ~102 nm over the whole sample with the RMS thickness inhomogeneity of 2.8 %, which is in striking contrast to 11.9%. Meanwhile, we obtain the growth rate of ~102 nm/h for GaN films grown at the temperature of 750 ºC. Evidently, the application of an optimal laser rastering program in PLD can effectively enhance the homogeneity of as-grown GaN films. Furthermore, these GaN films show the much better thickness homogeneity than the GaN films grown by traditional PLD as well as the combination of ECR-PEMOCVD and radio-frequency magnetron sputtering. [2-4, 22-28]

In-situ RHEED, SEM and AFM measurements are deployed to further investigate the surface morphologies of as-grown GaN films. After annealing for 60 min, the atomically flat Cu (111) is achieved with sharp and clear RHEED patterns, as shown in Fig. 2a. These flat Cu (111) substrates are beneficial to the subsequent growth of AlN buffer layer. Fig. 2b is the typical RHEED patterns for as-grown ~950-nm-thick AlN films on Cu (111) substrates at 550 ºC, which indicates that single-crystalline AlN films with very flat surface have been obtained on Cu(111) substrates. Meanwhile, Fig. 2c is the sharp and clear RHEED patterns for ~102-nm-thick GaN films grown on the ~950-nm-thick AlN buffer layer at 750 ºC, which reveals that single-crystalline GaN films with smooth surfaces have been grown. Furthermore, from the RHEED measurements, the in-plane epitaxial relationship of GaN[11-20]//AlN[11-20]//Cu[1-10] can be found. This result indicates that the lattice mismatch between AlN and Cu is 21.8%. The SEM image for ~102-nm-thick GaN films grown at 550 ºC is shown in Fig. 2d, where one can identify the very rough surface with many islands on the surface with the surface RMS roughness of 7.5 nm measured by AFM. If the growth temperature is increased to 750 ºC, it exhibits very smooth surface which are typical features for GaN films, as shown in Fig. 2e. Actually, the AFM measurement reveals the surface RMS roughness of 2.3 nm, as shown in Fig. 2f. Evidently, the growth temperature for GaN films is of paramount importance in obtaining high-quality GaN films. The higher growth temperature is beneficial to the growth of higher-quality GaN films, because the higher temperature provides enough energy for the migration of GaN precursors on the substrates, and eventually leads to the formation of smoother film surface. Furthermore, the surface morphologies of GaN films achieved in this work are comparable with that grown by other groups.[2-4, 22-26] Meanwhile, the polarized light microscopy and FESEM measurements have revealed that crack-free GaN films can be obtained with a very small cooling rate of 3 ºC/min from growth temperature to room temperature due to the large coefficients in thermal expansion (CTE) mismatches between nitrides and Cu substrates.[31] Therefore, as for thin films, only by controlling the cooling rate, crack-free films can be obtained. In our case, the critical thickness for GaN films grown on Cu substrates is ~200 nm at the growth temperature of 750 ºC. As for thicker films, apart from controlling the cooling rate,[31] other techniques such as SiN_x interlayer and AlGaN step-graded buffer layer, are needed to grow crack-free films on Cu substrates.[34-37]

The structural properties of as-grown GaN films on Cu (111) substrates are studied by HRXRD. Fig. 3a shows a typical 2θ-ω scan. The peaks observed at 2θ=34.6° and 2θ=36.1° are the GaN (0002) and AlN (0002), respectively; while the peak found at 2θ=43.7° is ascribed to Cu (111).[38] These results demonstrate that the single-crystalline GaN (0002) films have been grown on Cu (111) substrates through growing single-crystalline AlN (0002) buffer layer with the out-of-plane epitaxial growth relationship of GaN(0001)//AlN(0001)//Cu(111). Fig.3b reveals the XRD φ scans for Cu (1-13), AlN (11-22) and GaN (11-22), and one can clearly identify the six-fold rotational peaks with the interval of 60° for all of them. On the one hand, this result confirms that hexagonal *c*-plane GaN films are epitaxially grown on Cu (111) substrates with hexagonal *c*-plane AlN buffer layer. On the other hand, it also shows that the in-plane epitaxial relationship for AlN and GaN films on Cu (111) substrates is GaN[11-20]//AlN[11-20]//Cu[1-10]. In other words, there are no 30° rotational domains in these films.

The crystalline quality of as-grown ~102-nm-thick GaN films is studied by X-ray rocking curves. It is known to us that the full width at half maximum (FWHM) value for (0002) is related to the screw dislocation density that is mainly generated from the different step height of the substrate; while the FWHM value for (10-12) is related to the edge and mixed dislocation densities that are mainly generated from the coalescence process among the disoriented individual islands.[1, 31] The crystalline quality for ~950-nm-thick AlN films is studied by XRD rocking curve.

The FWHMs for AlN (0002) and AlN (10-12) are 1.0º and 1.1º, respectively. These values are much smaller than our previous work of growing AlN films on Cu substrates,[31] and is good for the subsequent growth of GaN films. Figs. 4a and b are the typical X-ray rocking curves for GaN (0002) and GaN(10-12) grown on Cu (111) substrates at the growth temperature of 750 ºC with the ~950-nm-thick AlN buffer layer, which show that the FWHMs for GaN(0002) and GaN(10-12) are 1.0° and 1.2°, respectively, corresponding to the dislocation density of ~10^{11}-10^{12} cm^{-2}.[1] Meanwhile, these results are slightly better than the results reported by other groups.[2-4, 24-28] Nevertheless, the crystalline quality of GaN films is much poorer than that grown on sapphire substrates, which partly due to the poor quality of Cu substrate for the FWHM value of Cu (111) X-ray rocking curve is as high as 0.8° and corresponds to a screw dislocations densities of ~10^{11} cm^{-2}. These dislocations may propagate into the AlN and GaN epitaxial layers and eventually deteriorate the crystalline quality of GaN films.[12, 39]

The temperature dependence of FWHMs for GaN films grown at temperature ranging from 550 to 750 ºC is also studied. From Fig. 4c, one can clearly find the FWHMs for both GaN(0002) and GaN(10-12) are 2.0° and 2.5° at 550 ºC, respectively; and are gradually decreased to 1.0° and 1.2° at 750 ºC, respectively. We attribute this to the higher growth temperature, which enhances the migration of GaN precursors on the surface, and eventually benefits to the growth of higher-quality GaN films. [19, 31]

In order to further investigate the strain state in as-grown ~102-nm-thick GaN films. The reciprocal space mappings (RSMs) of GaN (0002) and (10-15) planes are measured. Fig. 5a indicates the GaN (0002) RSM, which once again confirms the out-of-plane epitaxial growth relationship of GaN(0001)//AlN(0001)//Cu(111) measured by XRD 2θ-ω scan. From the GaN (10-15) RSM, one can identify the skew symmetry of GaN (10-15) and AlN (10-15), Furthermore, the lattice parameters for as-grown AlN and GaN films can be obtained of a_{AlN}= 0.3104 nm, c_{AlN}= 0.4985 nm, a_{GaN}= 0.3172 nm, c_{GaN}= 0.5192 nm, respectively. These mean that the as-grown AlN buffer layer is about 0.19% compressive along its *a*-axis, and is about 0.060% tensile along its *c*-axis; while as-grown GaN is about 0.53% compressive along its *a*-axis, and is about 0.058% tensile along its *c*-axis.[1, 40] In other words, we have obtained almost fully relaxed GaN films on Cu (111) substrates through growing of nearly fully relaxed AlN buffer layer.

The structural properties of GaN/AlN/Cu are studied by HRTEM and selected area electron diffraction (SAED). Fig. 6a is the cross-sectional TEM image for GaN films grown on Cu (111) substrates with AlN buffer layer at 750 ºC. We can clearly find that the thickness for as-grown AlN buffer layer and GaN films are ~950 and ~102 nm, respectively, illustrated by the black dashed lines in Fig. 6a. These results are well consistent with the white-light interferometry measurement. The cross-sectional HRTEM is deployed to further study the interfacial properties of AlN/Cu and AlN/GaN hetero-interfaces, as shown in Figs. 6b and c. From Fig.6b, we can find that there is no interfacial layer existing between AlN films and Cu substrates, which is much better than our previous result of AlN/Cu hetero-interfaces.[31] We ascribe this to the growth of AlN films at appropriate nitrogen pressure when compared with our previous report,[31] which can effectively reduce the diffusion of Cu atoms from substrates and enhance the migration of AlN precursors on the Cu surface, and thereby benefit to the growth of AlN films.[41-43] Detailed study on the TEM images with theoretical crystallography helps us to find another epitaxial growth relationship between AlN films and Cu substrates is of AlN[01-10]//Cu[11-2], as shown in Fig. 6b. The SAED image for AlN/Cu is shown in Fig. 6c, where the epitaxial relationships of AlN (0001)//Cu(111) and AlN[11-20]//Cu[1-10] can be deduced. Furthermore, we also study the interfacial properties of AlN/GaN hetero-interfaces grown at 550 and 750 ºC, as shown in Figs. 6d-e. There is an interfacial layer existing between AlN buffer layer and GaN film with the thickness of ~1.5 nm (about 4-5 monolayers) when the GaN films are grown at 550 ºC, as shown in Fig. 6d. There is no interfacial layer existing between AlN buffer layer and GaN film when the GaN films are grown at 750 ºC, as shown in Fig. 6e. These may be attributed to the different lattice and CTE mismatches between AlN and GaN at different temperatures.[44-51] Due to the lattice and CTE mismatches between AlN and GaN, the stress is formed in the AlN/GaN interface during the initial growth.[12-13] The stressed films may attempt to relieve stress by the formation of dislocations.[42] These dislocations would lead to the nonuniform diffusion of nitrogen and Ga plasmas on the interface during the further growth, and eventually result in the formation of interfacial layer.[44-45] In our case, the lattice and CTE mismatches between AlN and GaN at higher growth temperature of 750 ºC are much smaller than that at lower growth temperature of 550 ºC,[31, 50-51] which results in the formation of less stressed GaN films at higher growth temperature of 750 ºC. These GaN films tend to the uniform growth and lead to the absence of the interfacial layer.[44, 52-53] Meanwhile, the epitaxial growth relationship between AlN and GaN is of AlN [01-10]//GaN[01-10] also can be obtained. Therefore, we therefore obtain another epitaxial growth relationship of GaN[01-10]//AlN[01-10]//Cu[11-2]. By studying the electron diffraction directions, the in-plane epitaxial alignment of GaN[11-20]//AlN[11-20]//Cu[1-10] can be obtained, as shown in Figs. 6b and d, which is well consistent with XRD φ scans and agrees with the result reported by S. Inoue *et al.*[4]

4. Conclusions

In summary, we have successfully grown homogeneous and high-quality GaN films on Cu(111) subsrates with an in-plane alignment of GaN[11-20]//AlN[11-20]//Cu[1-10] by PLD. The surface morphologies and structrual properties of as-grown ~102-nm-thick GaN films are studied in detail. We find that the GaN films grown with optimized laser rastering exhibit excellent thickness uniformity with the RMS thickness inhomogeneity less than 2.8%, which is in striking contrast to 11.9% grown by traditional PLD. Meanwhile, the GaN films grown at 750 ºC show very flat surface with the surface RMS roghness of 2.3 nm, and the as-grown ~102-nm-thick GaN films are almost fully relaxed only with an in-plane compresive strain of 0.53%. There is no interfaical layer existing between AlN buffer layer and GaN film when the GaN films are grown at 750 ºC. While GaN films grown at lower temperature show the poorer surface morphologies and structural properties. We tentatively attribute these results mainly to two aspects. One is the application of laser rastering technology, and the other is suitable growth temperature. The former engineers the incident angles and the locations on the substrate of precursors, which results in a statistically homogeneous distribution of precursors on the substrates, and eventually leads to homogeneous films. The latter provides enough energy for the migration of precursors on the substrates, enhances the grwoth of films, and evetually benefits to the growth of high-quality films. Although homeogeneous and crack-free GaN films with high-quality have been achieved, furture work should be focused on the furthmer improvement of the GaN crystalline quality to meet the requirement of GaN-based devices. Neverthless, this achievement of homogeneous and high-quality GaN films on Cu(111) substrates is of great improtance for the future application of high-power GaN-based optoelectronic devices.

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References

[1] W. L. Wang, H. Yang and G. Q. Li, *J. Mater. Chem. C*, 2013, **1**, 4070-4077.

[2] S. Inoue, K. Okamoto, T. Nakano, J. Ohta and H. Fujioka, *Appl. Phys. Lett.*, 2007, **91**, 201920.

[3] K. Okamoto, S. Inoue, T. Nakano, J. Ohta and H. Fujioka, *J. Cryst. Growth*, 2009, **311**, 1311-1315.

[4] S. Inoue, K. Okamoto, N. Matsuki, T. -W. Kim and H. Fujioka, *Appl. Phys. Lett.*, 2006, **88**, 261910.

[5] S. A. Kukushkin, A.V. Osipov, V. N. Bessolov, B. K. Medvedev, V. K. Nevolin and K. A. Tcarik, *Rev. Adv. Mater. Sci.*, 2008, **17**, 1-32.

[6] S. I. Kim, *Solid State Electron.*, 2005, **49**, 1153-1157.

[7] Y. J. Lin, *Appl. Phys. Lett.*, 2004, **84**, 2760-2762.

[8] H. D. Zhang, Y. L. Shao, L. Zhang, X. P. Hao,Y. Z. Wu, X. Y. Liu, Y. B. Dai and Y. Tian, *CrystEngComm*, 2012, **14**, 4777-4780.

[9] Y. Tian, L. Zhang, Y. Z. Wu, Y. L. Shao, Y. B. Dai, H. D. Zhang, R. S. Wei and X. P. Hao, *CrystEngComm*, 2014, **16**, 2317-2322

[10] Y. L. Shao, Y. B. Dai, X. P. Hao, Y. Z. Wu, L. Zhang, H. D. Zhang and Y. Tian, *CrystEngComm*, 2014, **16**, 4100-4107.

[11] L. Zhang, Y. L. Shao, X. P. Hao, Y. Z. Wu, H. D. Zhang, S. Qu, X. F. Chen and X. G. Xu, *CrystEngComm*, 2011, **13**, 5001-5004.

[12] L. Liu and J. H. Edgar, *Mater. Sci. Eng. R*, 2002, **37**, 61-127.

[13] R. C. Dorf, Handbook of engineering ta bles, C RC Press LLC, Boca Rat on, London, New York, Washington, D .C., 2003, pp.189-190.

[14] T. Ueda, M. Ishida, S. Tamura, Y. Fujimoto, M. Yuri, T. Saito and D. Ueda, Phy. Stat. Sol. (c), 2003, **0**, 2219-2222.

[15] C. F. Chu, F. L. Lai, J. T. Chu, C. C. Yu, C. F. Lin, H. C. Kuo and S. C. Wang, *J. Appl. Phys.*, 2004, **95**, 3916-3922.

[16] Y. J. Sun, T. J. Yu, C. Y. Jia, Z. Z. Chen, P. F. Tian, X. N. Kang, G. J. Lian, S. Huang and G. Y. Zhang, *Chin. Phys. Lett.*, 2010, **27**, 127303.

[17] G. Q. Li, T. W. Kim, S. Inoue, K. Okamoto and H. Fujioka, *Appl. Phys. Lett.*, 2006, **89**, 241905.

[18] S. Inoue, K. Okamoto, N. Matsuki, T. W. Kim and H. Fujioka, *J. Cryst. Growth*, 2006, **289**, 574-577.

[19] H. Yang, W. L. Wang, Z. L. Liu and G. Q. Li, *J. Phys. D: Appl. Phys.*, 2013, **46**, 105101.

[20] R. Dietsch, Th. Holz, H. Mai, C. F. Meyer, R. Scholz and B. Wehner, *Appl. Surf. Sci.*, 1998, **127-129**, 451-456.

[21] R. Dietsch, Th. Holz, D. Weißbach and R. Scholz, *Appl. Surf. Sci.*, 2002, **197-198**, 169-174.

[22] K. Okamoto, S. Inoue, N. Matsuki, T. -W. Kim, J. Ohta1, M. Oshima, H. Fujioka and A. Ishii, *Appl. Phys. Lett.*, 2008, **93**, 251906.

[23] M. Oseki, K. Okubo, A. Kobayashi, J. Ohta and H. Fujioka, *Sci. Rep.*, 2014, **4**, 3951.

[24] T. -W. Kim, N. Matsuki, J.Ohta and H. Fujioka, *Jpn. J. Appl. Phys.*, 2006, **45**, L 396-L 398.

[25] Y. M. Liu, F. W. Qin, D. Zhang, J. M. Bian, Y. Zhao, E. P. Wang, S. Wang, M. M. Zhong and Z. H. Ju, *J. Cryst. Growth*, 2013, **368**, 92-96.

[26] F. W. Qin, M. M. Zhong, C. Wang, Y. M. Liu, J. M. Bian, E. P. Wang, H. Wang and D. Zhang, *J. Mater. Sci. Mater. Electron*, 2013, **24**, 5069-5074.

[27] M. M. Zhong, F. W. Qin, Y. M. Liu, C. Wang, J. M. Bian, E. P. Wang, H. Wang and D. Zhang, *J. Alloy. Compd.*, 2014, **583**, 39-42.

[28] Y. Zhao, F. W. Qin, Y. Z. Bai, Z. H. Ju, Y. Zhao, X. H. Zhang, S. M. Li, D. Zhang, J. M. Bian, and Y. Li, *Vacuum*, 2013, **92**, 77-80.

[29] H. Yang, W. L. Wang, Z. L. Liu and G. Q. Li, *CrystEngComm*, 2013, **15**, 7171-7176.

[30] S. J. Guilfoyle, M. D. Crapper, M. Lovelady and M. Petty, *J. Magn. Magn. Mater.*, 1999, **198-199**, 113-115.

[31] W. L. Wang, W. J. Yang, Z. L. Liu, Y. H. Lin, H. Yang, F. L. Gao and G. Q. Li, *Appl. Surf. Sci.*, 2014, **294**, 1-8.

[32] J. P. Hespanha, Root-Mean-Square Gains of Switched Linear Systems, *IEEE T. Automat. Contr.*, 2003, **48**, 2040-2045.

[33] T. O. Salmon and C. van de Pol, *J. Catarct. Refract. Surg.*, 2006, **32**, 2064-2074.

[34] J. L. Liu, J. L. Zhang, Q. H. Mao, X. M. Wu and F. Y. Jiang, *CrystEngComm*, 2013, **15**, 3372-3376.

[35] D. Zhu, D. J. Wallis and C. J. Humphreys, *Rep. Prog. Phys.*, 2013, **76**, 106501.

[36] X. N. Yan, M. D. Qian, L. R. Gao, X. H. Yang, Y. Dai, X. Y. Yan and G. H. Ma, *Opt. Express*, 2013, **21**, 31852-31861.

[37] M. Wei, X. L. Wang, X. Pan, H. L. Xiao, C. M. Wang, M. L. Zhang and Z. G. Wang, *J. Phys.: Conf. Ser.*, 2011, **276**, 012094.

[38] M. Chmielov, J. Seidlerov and Z. Weiss, *Corros. Sci.*, 2003, **45**, 883-889.

[39] W. L. Wang, S. Z. Zhou, Z. L. Liu, W. J. Yang, Y. H. Lin, H. R. Qian, F. L. Gao and G. Q. Li, *Mater. Res. Express*, 2014, **1**, 025903.

[40] M. A. Moram and M. E.Vickers, *Rep. Prog. Phys.*, 2009, **72**, 036502.

[41] H. Yang, W. L. Wang, Z. L. Liu, W. J. Yang and G. Q. Li, *CrystEngComm*, 2014, **16**, 3148-3154.

[42] W. L. Wang, W. J. Yang, Z. L. Liu, Y. H. Lin, S. Z. Zhou, H. R. Qian, F. L. Gao and G. Q. Li, *CrystEngComm*, 2014, **16**, 4100-4107.

[43] W. L. Wang, H. Yang and G. Q. Li, *CrystEngComm*, 2014, **15**, 2669-2674.

[44] M. Tang, K. W. EvansLutterodt, M. L. Green, D. Brasen, K. Krisch, L. Manchanda, G. S. Higashi and T. Boone, *Appl. Phys. Lett.*, 1994, **64**, 748-750.

[45] T. W. Kim, H. L. Park, J. Y. Lee and H. J. Lee, *Appl. Phys. Lett.*, 1994, **65**, 2597-2599.

[46] E. P. Gusev, H. C. Luand, T. Gustafsson and E.Garfunkel, *Phys. Rev. B*, 1995, **52**(3), 1759-1775.

[47] F. SchäHlert, D. Többenz, H. J. Herzogt, G. Abstreiterz and B Holländer, *Semicond. Sci. Technol.*, 1992, **7**, 260-266.

[48] Z. X. Cao, Thin films growth, Woodhead publishing limited, Oxford, Cambridge Philadelphia, New Delhi, 2011.

[49] S. M. Wang, T. G. Andersson and M. J. Ekenstedt, *Appl. Phys. Lett.*, 1992, **61**, 3139-3141.

[50] W. M. Yim and R. J. Paff, J. Appl. Phys., 1974, **45**, 1456-1457.

[51] M. Leszczynski, T. Suski, H. Teisseyre, P. Perlin, I. Grzegory, J. Jun, S. Porowski and T. D. Moustakas, J. Appl. Phys., 1994, **76** (8), 4909-4911.

[52] E A. Irene, E. Tierney and J. Angilello, *J. Electrochem. Sot.*, 1982, **129**, 2594-2597.

[53] S. Tanaka, Y. Kawaguchi, N. Sawaki, M. Hibino and K. Hiramatsu, *Appl. Phys. Lett.*, 2000, **76**, 2701-2703.

Figure Captions

Fig. 1. (a) A schematic photograph of as-grown GaN films with rastering settings,[31] and (b) the thickness distribution for 1×1 cm^2 GaN films grown on homogeneous AlN buffer layer after 60 min PLD growth at 750 ºC.

Table I. The relationship between the different laser raster rate and the thickness inhomogeneity of as-grown GaN thin films.

Fig. 2. Surface morphologies of GaN films grown on Cu substrates with AlN buffer layer. Typical RHEED patterns for (a) Cu substrates, (b) ~950-nm-thick AlN buffer layer, and (c) ~102-nm-thick GaN films. SEM image for ~102-nm-thick GaN films grown on the AlN buffer layer at (d) 550 ºC, and (e) 750 ºC. (f) AFM image for ~102-nm-thick GaN films grown at 750 ºC.

Fig. 3. (a) Typical XRD 2θ-ω scan for GaN (0002), (b) XRD φ scans for Cu (1-13), AlN (11-22) and GaN (11-22).

Fig. 4. XRD rocking curves for ~102-nm-thick (a) GaN (0002), (b) GaN (10-12) films grown on Cu(111) substrates with AlN buffer layer at 750 ºC. (c) Temperature dependence of FWHMs for GaN (0002) and GaN (10-12) rocking curves at the temperature range from 550 to 750 ºC.

Fig. 5. RSMs of (a) GaN (0002) and (b) GaN (10-15) for the ~102-nm-thick GaN films grown on Cu (111) substrates with ~950-nm-thick AlN buffer layer at the growth temperature of 750 ºC.

Fig. 6. Cross-sectional TEM for GaN films grown on Cu (111) substrates with AlN buffer layer under two beam direction of g=[11-20]. (a) A bright cross-sectional TEM image for GaN films grown on Cu (111) substrates at 750 ºC with low magnification. (b) Cross-sectional HRTEM image for AlN/Cu hetero-interfaces grown at 550 ºC, and its (c) SAED image, where the spots marked in red are the planes of Cu and the spots marked in white are the planes of AlN. Cross-sectional HRTEM images for AlN/GaN hetero-interfaces grown at (d) 550, and (e) 750 ºC.

Fig. 1.

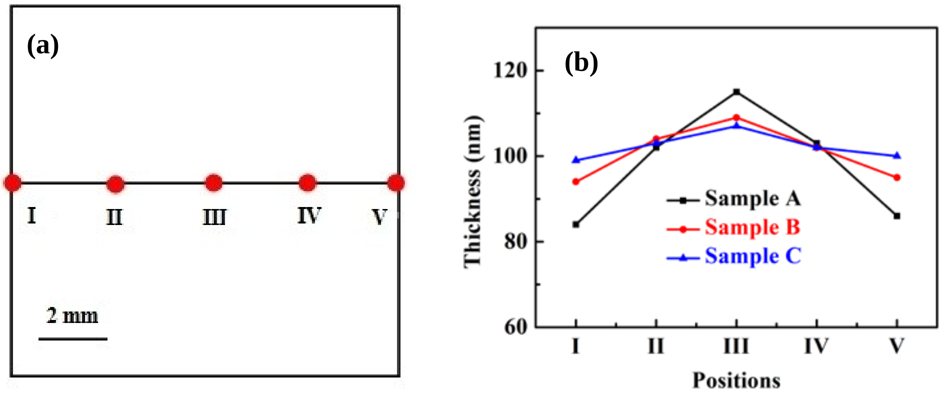
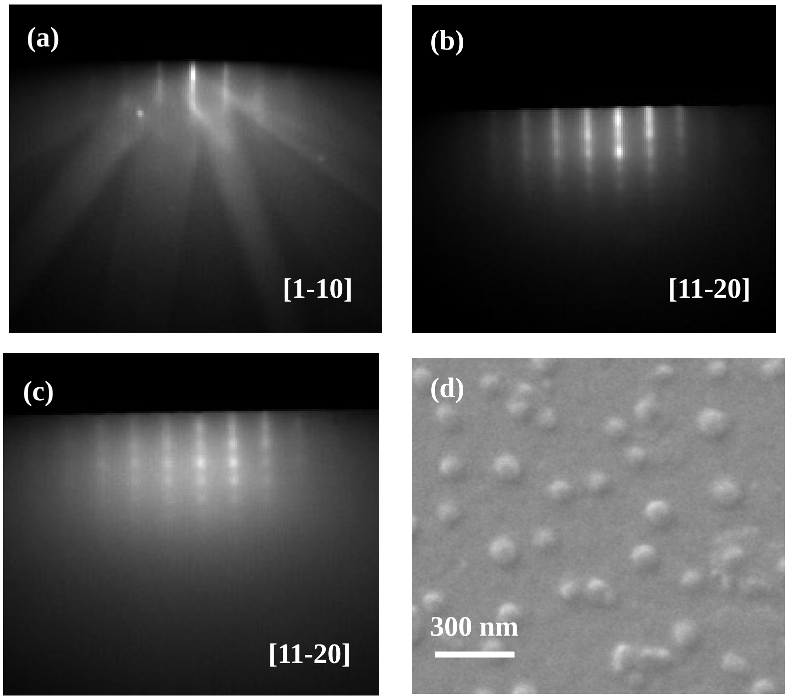


Table 1.

Samples	Laser raster rate			Thickness inhomogeneity
	S1 (steps/s)	S2 (steps/s)	S3 (steps/s)	RMS (%)
A	0	0	0	11.9
B	100	100	100	5.6
C	100	60	20	2.8

Fig. 2.



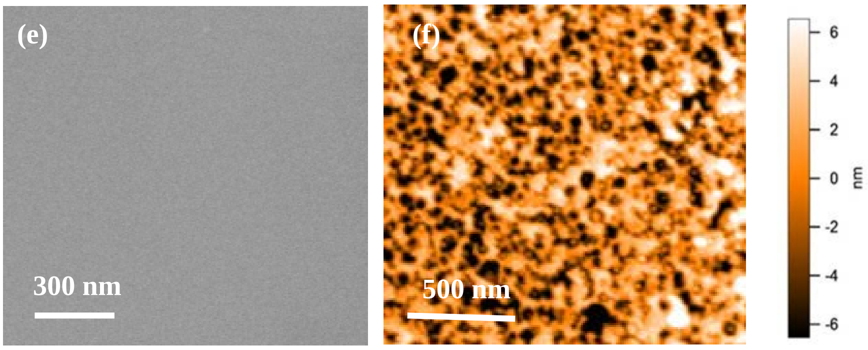

(e)
300 nm
(f)
500 nm
6
4
2
0
-2
-4
-6
nm

Fig. 3.

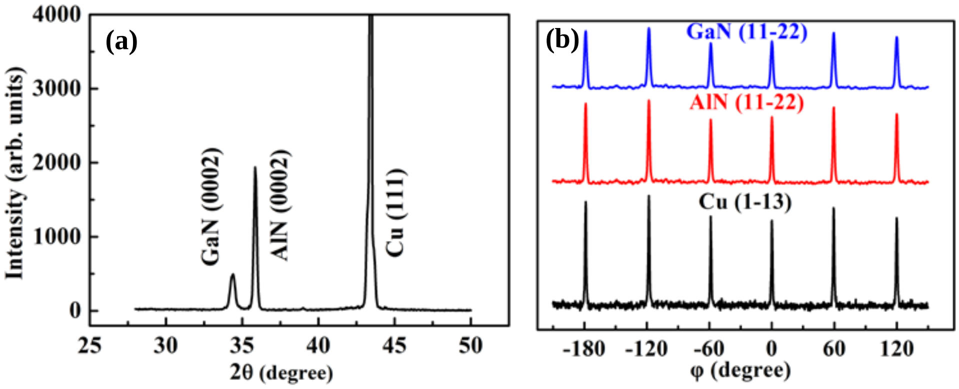

(a)
4000
3000
2000
1000
0
Intensity (arb. units)
GaN (0002)
AlN (0002)
Cu (111)
25
30
35
40
45
50
2θ (degree)
(b)
GaN (11-22)
AlN (11-22)
Cu (1-13)
-180
-120
-60
0
60
120
φ (degree)

Fig. 4.

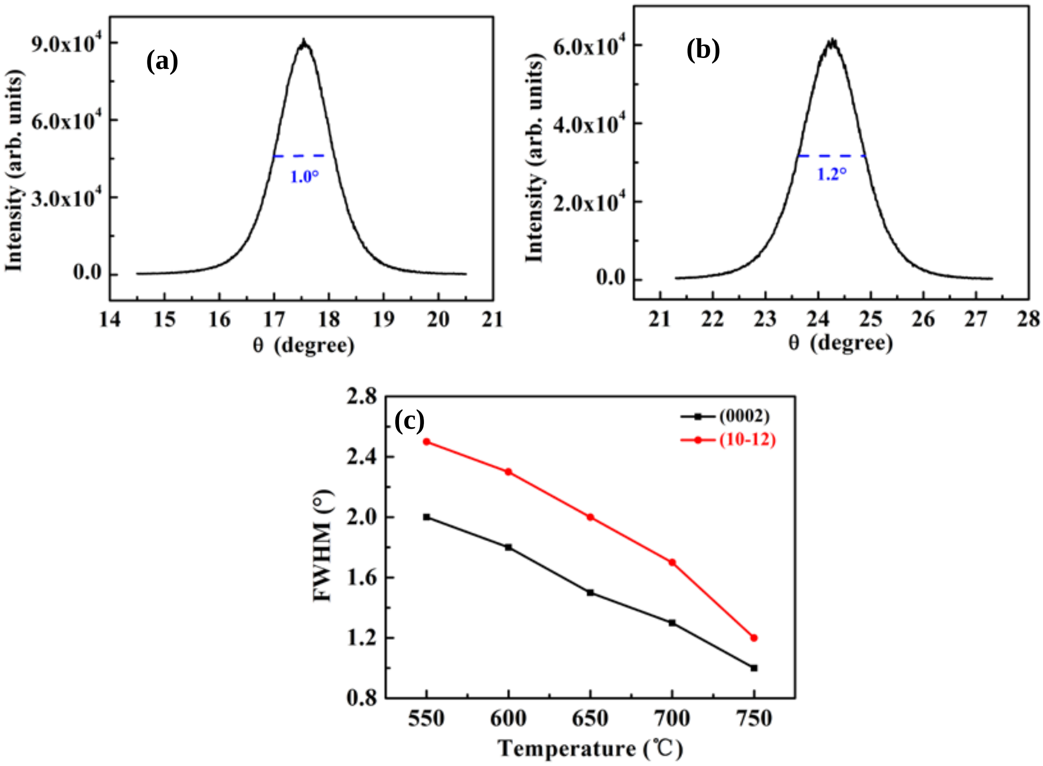

(a)
9.0x10^4
6.0x10^4
3.0x10^4
0.0
Intensity (arb. units)
1.0°
14
15
16
17
18
19
20
21
θ (degree)
(b)
6.0x10^4
4.0x10^4
2.0x10^4
0.0
Intensity (arb. units)
1.2°
21
22
23
24
25
26
27
28
θ (degree)
(c)
2.8
2.4
2.0
1.6
1.2
0.8
FWHM (°)
(0002)
(10-12)
550
600
650
700
750
Temperature (℃)

Fig. 5.

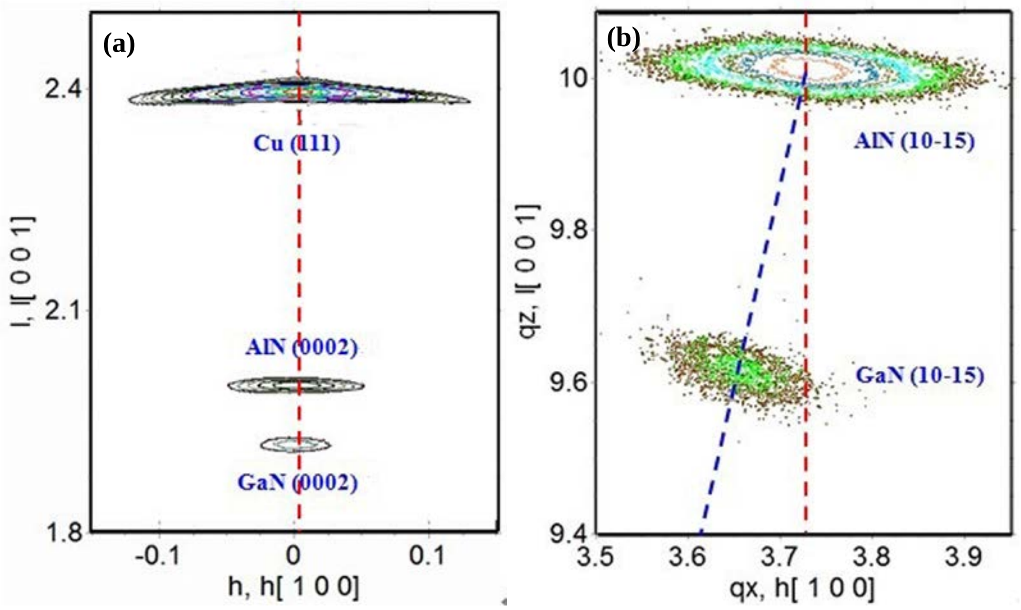
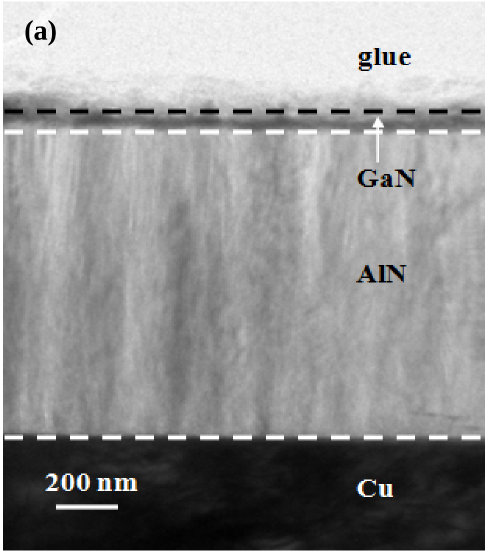

(a)
Cu (111)
AlN (0002)
GaN (0002)
2.4
2.1
1.8
l, l[0 0 1]
-0.1
0
0.1
h, h[1 0 0]
(b)
AlN (10-15)
GaN (10-15)
10
9.8
9.6
9.4
qz, l[0 0 1]
3.5
3.6
3.7
3.8
3.9
qx, h[1 0 0]

Fig. 6.


(a)
glue
GaN
AlN
Cu
200 nm

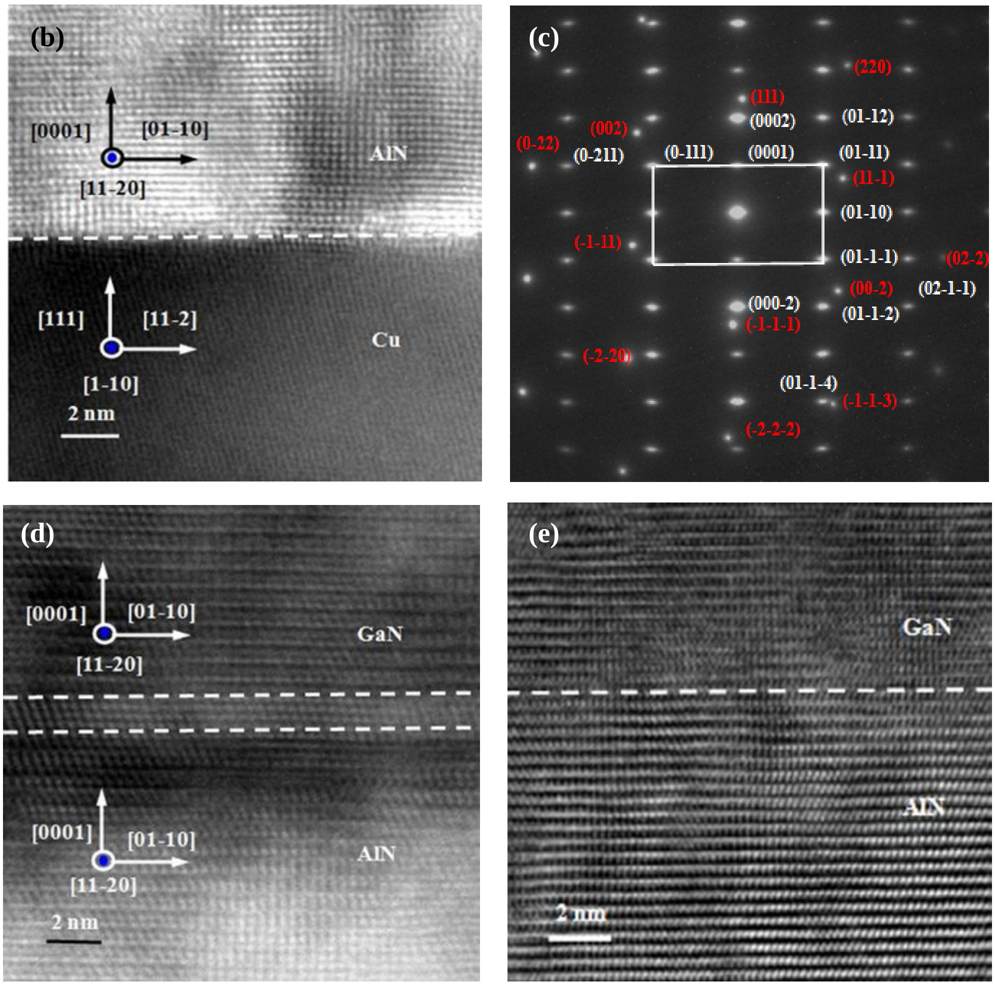

(b)
[0001]
[01-10]
[11-20]
AlN
[111]
[11-2]
[1-10]
Cu
2 nm
(c)
(220)
(111)
(0002)
(01-12)
(002)
(0-22)
(0-211)
(0-111)
(0001)
(01-11)
(11-1)
(01-10)
(-1-11)
(01-1-1)
(02-2)
(00-2)
(02-1-1)
(000-2)
(01-1-2)
(-1-1-1)
(-2-20)
(01-1-4)
(-1-1-3)
(-2-2-2)
(d)
[0001]
[01-10]
[11-20]
GaN
[0001]
[01-10]
[11-20]
AlN
2 nm
(e)
GaN
AlN
2 nm

Table of contents:

Title: Synthesis of homogeneous and high-quality GaN films on Cu (111) substrates by pulsed laser deposition

Descriptions: The homogeneous and high-quality GaN films have been grown by pulsed laser deposition with homogeneous AlN buffer layer. By optimizing laser rastering program and epitaxial growth temperature, high-quality GaN films with a root-mean-square thickness inhomogeneity less than 2.8% have been obtained.