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Effect of TMGa flux on GaN films deposited on Ti coated on glass substrates at low temperature

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Highly *c*-axis-oriented GaN films were deposited on Ti coated glass substrates using low temperature electron cyclotron resonance plasma enhanced metal organic chemical vapor deposition system (ECR-PEMOCVD) with trimethyl gallium (TMGa) as gallium source. The influence of TMGa flux on the properties of GaN films were systematically investigated by reflection high energy electron diffraction (RHEED), X-ray diffraction analysis (XRD), atomic force microscopy (AFM) and Raman scattering. The GaN film with small surface roughness and high *c*-axis preferred orientation was successfully achieved at the optimized TMGa flux of 1.0 sccm. The ohmic contact characteristic between GaN and Ti layer was clearly demonstrated by the near-linear current-voltage (*I-V*) curve. The GaN/Ti/glass structure has great potential to dramatically improve the scalability and reduce the cost of solid-state lighting light emitting diodes.

GaN, low-temperature deposited, glass substrates, Ti film, ECR-PEMOCVD

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Gallium nitride (GaN) is considered to be an attractive semiconductor for its wide and direct energy band gap, which makes it be suitable for light emitting diodes (LEDs) and laser diodes (LDs) [1,2]. Furthermore, the excellent thermal stability of GaN also makes it a promising material for high-temperature and high-power semiconductor devices. The nitride alloys with band gaps ranged from 1.9 to 6.2 eV could be obtained with GaN, AlN and InN; thus devices operated in a wide range wavelength can be achieved. Especially, conventional light sources are currently being replaced by GaN-based solid-state lighting due to its advantages of higher reliability, longer lifetime and lower power consumption. At present, GaN are deposited mainly by high temperature metal organic chemical vapor deposition (MOCVD), mostly on a single-crystal sapphire or silicon carbon substrate, because bulk GaN crystals are not commercially available nowadays. Although the defect density is still very high due to a remaining lattice mismatch between GaN and the substrates, fortunately, GaN-based solid-state devices exhibit a peculiar capacity to emit light efficiently even in the presence of high defect density. Sapphire is the most common substrate for GaN epitaxy, but there are many disadvantages for sapphire to be a substrate. It is an electrically insulating material with a low thermal conductivity (about 25 W/(m K) at 100°C). Therefore, the performance of GaN based devices, especially high power devices, is often restricted by the poor electric conductivity and the low thermal conductivity of sapphire substrate. It seems that SiC is a good candidate for substrates to replace sapphire due to its less lattice mismatch (only 3.4%), wide band gap, high thermal conductivity, and excellent chemical durability. Unfortunately, SiC substrates are expensive and

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of small-area compared with sapphire substrates. On the contrary, metal is an ideal conductor of electricity and heat. So, several groups have deposited GaN films on sapphire substrates using conventional growth methods and then separated them from substrates by laser lift-off (LLO) technique, transferring the device layers to metal substrates [3,4]. To a certain extent, this technique has improved the performance of devices for the improvement in heat dissipation. However, LLO technique has caused a series of problems: On one hand, the fabrication process becomes quite complicated, and yields of these devices are decreased [5]; on the other hand, the soldering process can decrease the heat dissipation of substrates. Therefore, the development of a direct deposition of GaN on metal substrates is highly desired.

Currently, there are several reports on the use of copper [5] and silver [6] as substrates to epitaxial growth GaN films. Among various metals, Ti is considered to be one of the most promising substrates for the large area low cost GaN-based photonic devices due to its excellent properties such as its excellent electrical and thermal conductivity, as well as high optical reflection. These features are absolutely imperative for the subsequent GaN-based semiconductor devices. However, during the conventional deposition process, the high temperature that is necessary for decomposition of ammonia may cause serious interfacial reactions as well as thermal expansion coefficient mismatches between the GaN films and the metal substrates, and thus severely degrade the device performance. In order to suppress the adverse effects of high deposition temperatures, it was highly desirable to deposit crystalline GaN films on Ni metal substrate at low temperature.

In this work, highly *c*-axis-oriented GaN films are deposited on Ti coated glass substrates using ECR-PEMOCVD at low temperature, which has been successfully proved to be a feasible method to remarkably activate reactive energy of N_2 and hence GaN films can be grown by ECR-MOCVD at an extremely low temperature in our previous reports [7]. The low temperature growth of GaN films with ECR-PEMOCVD can be attributed to the enhanced kinetic energies of the film precursors, which assist the surface migration and reduce the interfacial reactions [8]. The influences of TMGa flux on the properties of as-grown GaN films were investigated systematically. The achievement will be especially attractive for large area high power GaN-based devices with excellent heat dissipation.

1 Materials and methods

1.1 Substrates

In this experiment, Ti coated films with thicknesses of about 600 nm were used as substrates, which were sputtered on glass substrates by direct current magnetron sputter system. Prior to growth Ti coated films, the glass substrates were cleaned ultrasonically with acetone, ethanol and deionized water for 10 min sequentially, dried with clean air and then introduced into the magnetron sputter reaction chamber. The samples were prepared at room temperature using dc sputtering deposition from a 99.99% Ti target and Ar of 99.9995% purity as a working gas (10 sccm). The base vacuum at the beginning of growth of each sample was lower than 1.2×10^{-3} Pa. Additionally, the distance between target and substrate was kept at 70 mm and the sputtering pressure is 1.0 Pa. The films were deposited at power of 30 W for 30 min. Finally, Ti samples were put into glove box filled with high-purity nitrogen gas.

1.2 The growth method of GaN thin films

GaN films were deposited on Ti coated glass substrates using an ECR-PEMOCVD system. Under the ECR plasma condition, the chemical reaction of gas and the deposit of GaN films are easy to achieve. Prior to growth, the substrate surface was cleaned by pure H_2 at room temperature for 3 min with H_2 flux of 80 sccm. Then, the surface of Ti films was nitridated by plasma gas with N_2 flux of 80 sccm at room temperature for 20 min. The nitridation process forms a TiN buffer layer on the surface of Ti coated films, and the buffer layer helps to lower the mismatch between Ti and GaN film. Trimethyl gallium (TMGa) and high-purity N_2 were employed as the source of Ga and N, respectively. The temperature of TMGa was kept at −14.1°C with semiconductor well and H_2 was used as the carrier gas. Before depositing GaN epitaxial layer, a GaN buffer layer was grown on Ti coated glass substrates at the room temperature for 30 min with thickness about 60 nm. The TMGa flux is 0.5 sccm and N_2 flux is 80 sccm. This low temperature buffer layer was expected to alleviate the lattice and thermal mismatches between Ti coated glass substrates and GaN films, and also used to supply nucleation centers to promote the crystalline quality of GaN films [9–11]. Additionally, N_2 flux was increased to 100 sccm by mass flow controller. Then the GaN films were grown at 380°C for 180 min. The TMGa flux varied from 0.6 to 1.4 sccm to investigate the effect of TMGa flux on the structure and property of GaN films. The thicknesses of the as-grown GaN films are about 680, 720, 851, 974, and 1027 nm, respectively. In order to decrease the thermal stress, the substrate temperature was reduced slowly to room temperature [12].

1.3 The test method of Ti substrates and GaN thin films

Ti substrates and as-grown GaN films were investigated by *in situ* reflection high-energy electron diffraction (RHEED) at 19 kV, X-ray diffraction (XRD) using a D/Max-2400 (Cu Kα, λ=0.154056 nm) and atomic force microscopy (AFM). In addition, Raman spectroscopy and the current-voltage (*I*-*V*) characteristic of Ti contacts to GaN are characterized at room temperature.

2 Results and discussion

2.1 The properties of Ti substrates

Figure 1(a) shows the RHEED pattern of Ti film, which was sputtered on glass. It can be observed that two slight rings appeared in the pattern. The XRD curve was shown in Figure 1(b), and there is a low peak appeared near 35.3°, which is characteristic of the Ti (100) plane. Combining the RHEED pattern and XRD curve, we can conclude that the Ti film exhibits a polycrystalline structure with (100) orientation. Figure 1(c) shows the AFM image of Ti substrate, and the surface root mean square (RMS) is 5.35 nm.

2.2 RHEED measurement of GaN films

RHEED system makes it easier to investigate the crystallinity of GaN film. Figure 2 shows the RHEED patterns of as-grown GaN films deposited on Ti coated glass substrates at different TMGa flux varied from 0.6 to 1.4 sccm. With the increase of TMGa flux from 0.6 to 1.0 sccm, the images of GaN film become clearer and brighter and the rings show disconnected tendency, and the disconnected rings gradually become isolated dots. However, when the TMGa flux continue to increase from 1.2 to 1.4 sccm, the dots get increasingly unclear and the pattern of TMGa flux 1.4 sccm becomes a mix of dots and rings. Among the five images, Figure 2(c) and (d) clearly shows the (002), (004), (103) and (105) diffraction dots. These results indicated that the TMGa flux of 1.0 and 1.2 sccm both are better parameters to obtain the GaN film with highly preferred orientation.

2.3 XRD measurement of GaN films

Figure 3 shows the grazing incidence XRD pattern of GaN films at different TMGa flux, and the flux changed from 0.6 to 1.4 sccm. It can be observed from the curves of GaN films that the stronger peak appeared near 34.6°, which are characteristic of the GaN (002) plane. This means that wutzite GaN was deposited on the Ti coated films. We roughly estimated the GaN (002) diffraction peak position, full width at half maximum (FWHM), grain size and lattice parameter of c-axis following the Scherrer equation [13]: $L=0.94\lambda/B\cos\theta$, where λ is the wavelength of the X-ray, θ

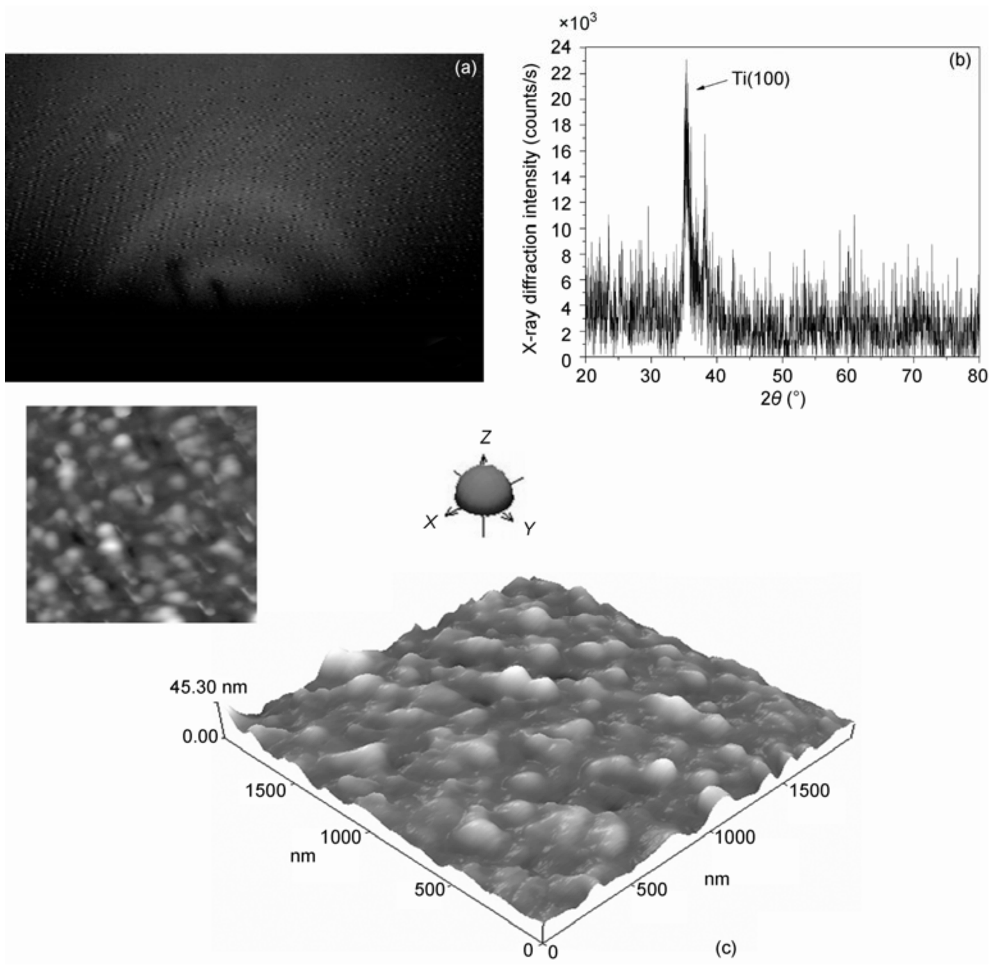

Figure 1 The RHEED (a), XRD (b) and AFM (c) patterns of the Ti coated film, respectively.

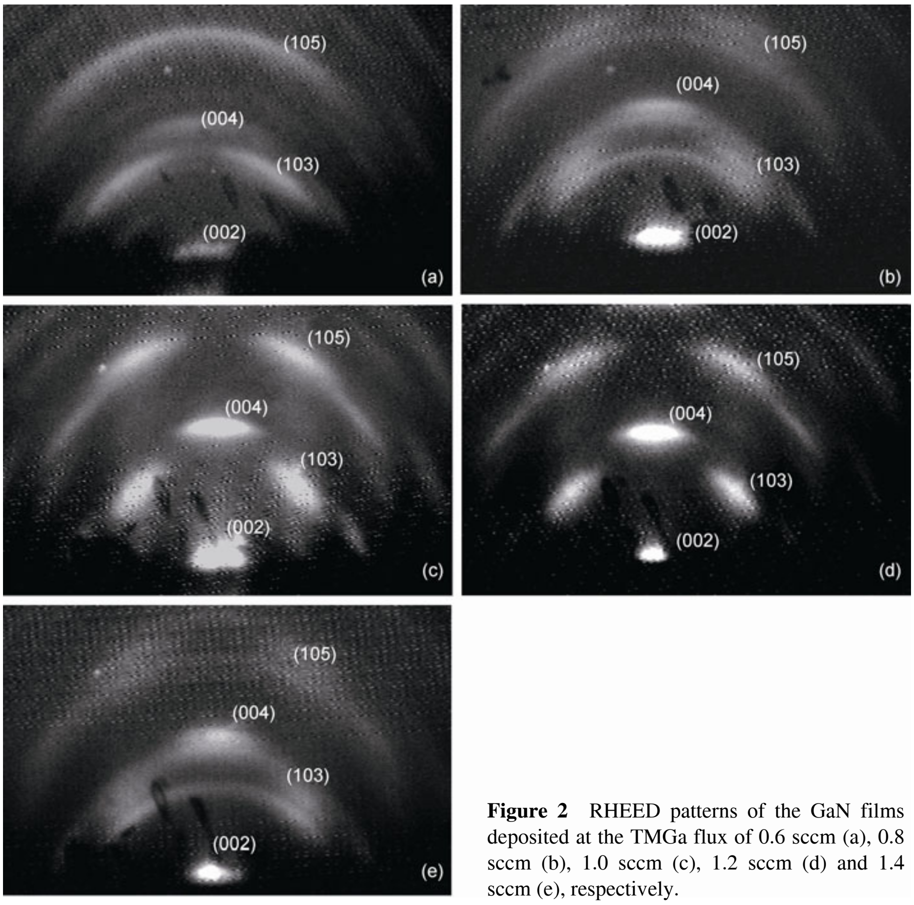

Figure 2 RHEED patterns of the GaN films deposited at the TMGa flux of 0.6 sccm (a), 0.8 sccm (b), 1.0 sccm (c), 1.2 sccm (d) and 1.4 sccm (e), respectively.

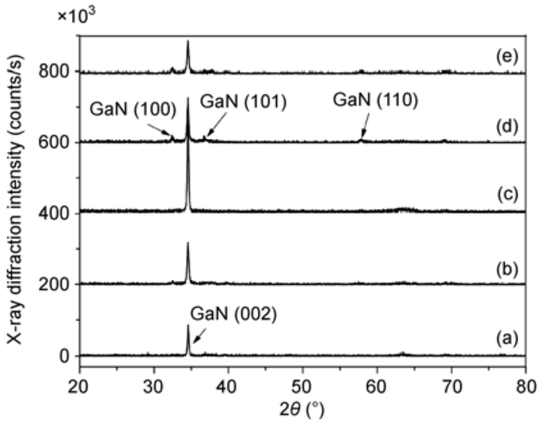

Figure 3 XRD spectrum of the GaN films deposited at the TMGa flux of 0.6 sccm (a), 0.8 sccm (b), 1.0 sccm (c), 1.2 sccm (d) and 1.4 sccm (e), respectively.

represents the Bragg angle of the X-ray diffraction peak and B is the FWHM of diffraction peak. The stress was investigated by the stress equation $\sigma = 2c_{13}^2 - c_{33}(c_{11}+c_{12})(c-c_0)/2c_{13}c_0$. The XRD pattern and the data of Table 1 suggest that the optimized TMGa flux is 1.0 sccm to obtain GaN film with the lowest FWHM, the maximum grain size and the minimum stress, and Table 1 also shows the *c*-axis lattice constant of sample c is 0.5184 nm, which is very close to the single crystalline GaN film (0.5185). There is a reasonable explanation for the changes of the data. When the TMGa flux lower than 1.0 sccm, Ga particles decreased over the substrate and the excess reactive nitrogen particles lead to the degradation of GaN crystal quality. When the TMGa flux is higher than 1.0 sccm, the excessive Ga particles produce Ga droplets and decrease the crystal quality of

Table 1 The GaN (0002) diffraction peak position, FWHM, lattice parameter of *c*-axis and grain size and stress

Sample	TMGa flux (sccm)	2θ (°)	FWHM (°)	Grain size (nm)	C_0 (nm)	Stress (GPa)
a	0.6	34.65	0.24	34	0.5169	2.81
b	0.8	34.54	0.23	36	0.5186	–0.24
c	1.0	34.60	0.20	42	0.5184	0.21
d	1.2	34.54	0.23	37	0.5186	–0.24
e	1.4	34.54	0.25	33	0.5187	–0.28

GaN film [12]. Therefore the optimum TMGa flux is 1.0 sccm.

2.4 AFM measurement of GaN films

Figure 4 presents the AFM patterns of the GaN films, which are deposited at different TMGa flux. With the TMGa flux increasing from 0.6 to 1.0 sccm, the surface roughness of GaN films gradually decrease. However, when the TMGa flux further increase from 1.0 to 1.4 sccm, the surface roughness of GaN films gradually increase. The primary reason for this tendency is as follows: proper TMGa flux

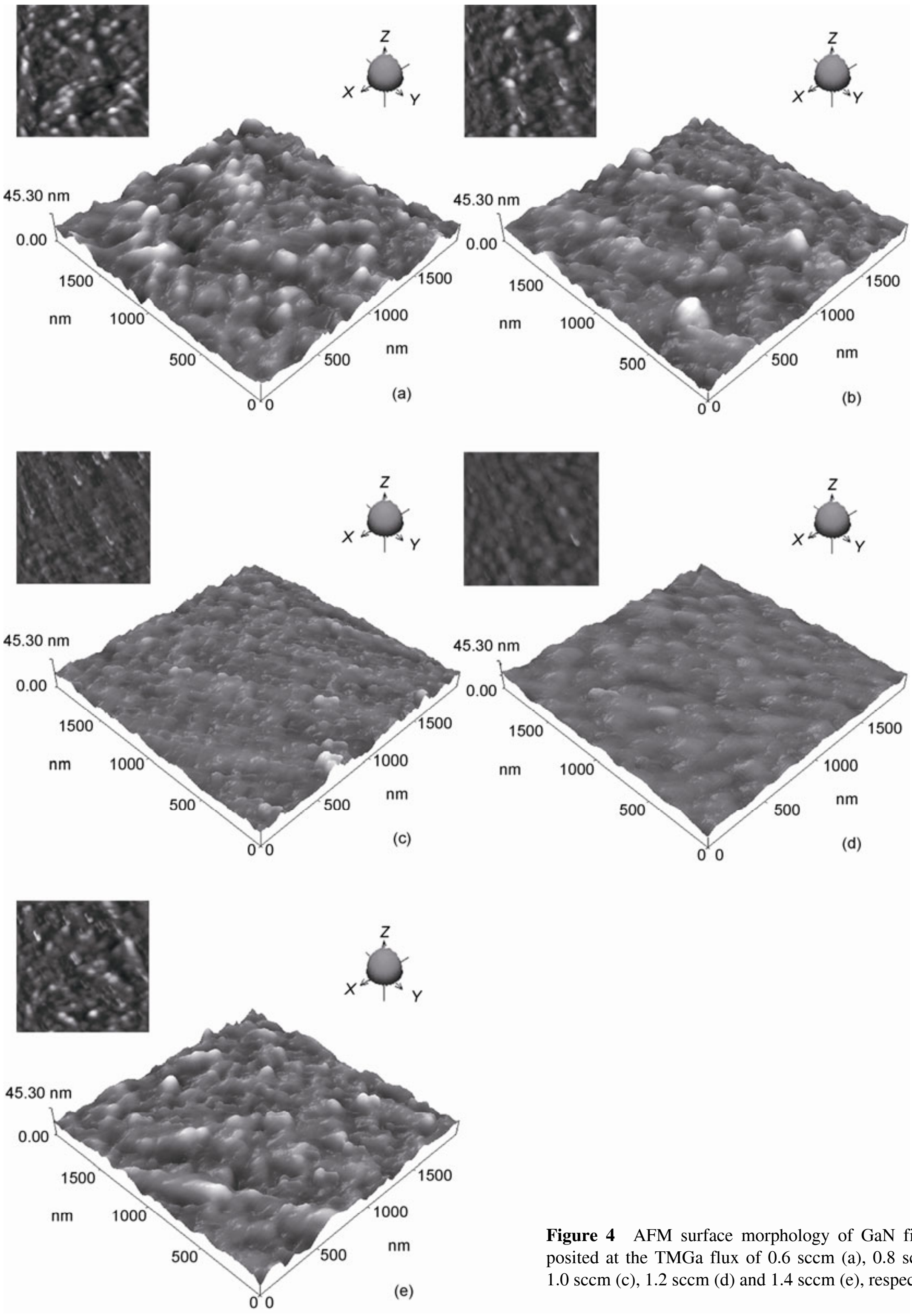

Figure 4 AFM surface morphology of GaN films deposited at the TMGa flux of 0.6 sccm (a), 0.8 sccm (b), 1.0 sccm (c), 1.2 sccm (d) and 1.4 sccm (e), respectively.

could promote the migration of surface atoms. On the contrary, excessive TMGa flux would damage the orderly growth of the surface atoms and the defects increased accordingly. When the TMGa flux is 0.6, 0.8, 1.0, 1.2 and 1.4 sccm, the RMS of GaN films is 6, 4.99, 3.13, 3.97 and 5.0 nm, respectively. Therefore, the polycrystalline GaN film with RMS of 3.13 nm was successfully deposited on Ti coated films, and it fully meets the requirements of surface roughness for semiconductor devices.

2.5 Raman spectra measurement

From Figure 5, it can be seen three peaks at about 230, 562.34 and 729.41 cm^{-1}. According to literatures, the broad peak at 230 cm^{-1} was attributed to titanium, the peak near 562.34 cm^{-1} is the E_2 (high) mode and the position of the peak near 729.41 cm^{-1} corresponds to the A_1 (LO) mode [14–18]. The Ti coated on glass substrates exhibit enhancement of Raman scattering, and it is so called surface-enhanced Raman spectroscopy (SERS). Therefore we can easily find the E_2 (high) mode. The reported peak positions of E_2 (high) and A_1 (LO) are 568 and 736 cm^{-1} [14,16], respectively. Therefore, in this experiment, the E_2 (high) and A_1 (LO) mode of GaN samples shifts towards the low-frequency side. The redshift may be attributed to strain relaxation effects. Therefore, a higher density of dislocations is expected in this sample [19]. It also should be noted that the growth of GaN is columnar, and this result is consistent with the X-ray diffraction data.

2.6 *I-V* characteristic measurement

Figure 6 presents the test structure of Ti contacts to GaN, which is grown at the 1.0 TMGa flux. As an electrode, bulk indium was pressed on the surface of GaN films and the ohmic contact resistivity between indium and GaN film is about 0.4 Ω cm^2. *I-V* characteristic of Ti/GaN film is shown in Figure 6(b). The curve exhibits near-linear characteristics at the current levels of 10 mA, indicating the ohmic properties of this contact. The resistivity for Ti/GaN film is about 2.6 Ω cm^2. Considering the extremely high background

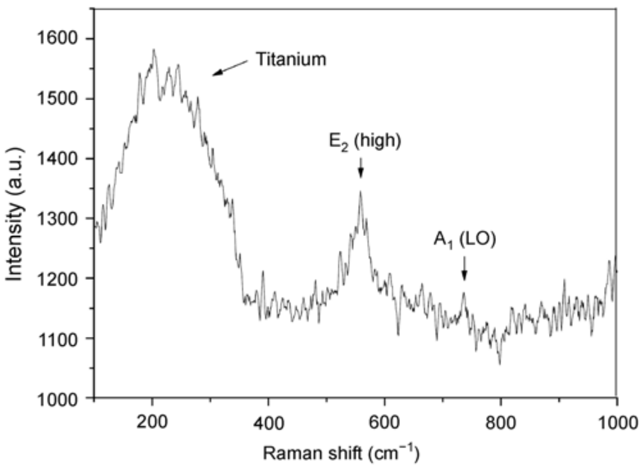

Figure 5 Raman spectra for the GaN layer of the sample c.

electron concentration of GaN buffer layer caused by the high density of donor defects, the interfacial potential barrier between GaN buffer layer and Ti film should be very low and interfacial tunneling probability would be very high, leading to the ohmic contact formation between metal and undoped-GaN without thermal treatment. The probability of GaN film contaminated by Ti from substrate was supposed to be rather low due to the extremely low growth temperature of ECR-PEMOCVD.

3 Conclusion

Highly *c*-axis-oriented GaN films have been deposited on Ti coated glass substrates by ECR-PEMOCVD. The effect of TMGa flux on the structure and property of GaN film were investigated systematically, and high *c*-orientation GaN film was achieved at the optimum TMGa flux of 1.0 sccm. At the same time, the *I-V* characteristics of metal contacts to GaN have been investigated and the curve showed the ohmic properties of this contact. These results indicate that it is possible to grow highly preferred GaN films on Ti coated glass substrates, and the development of large area high power GaN-based devices with excellent heat dissipation

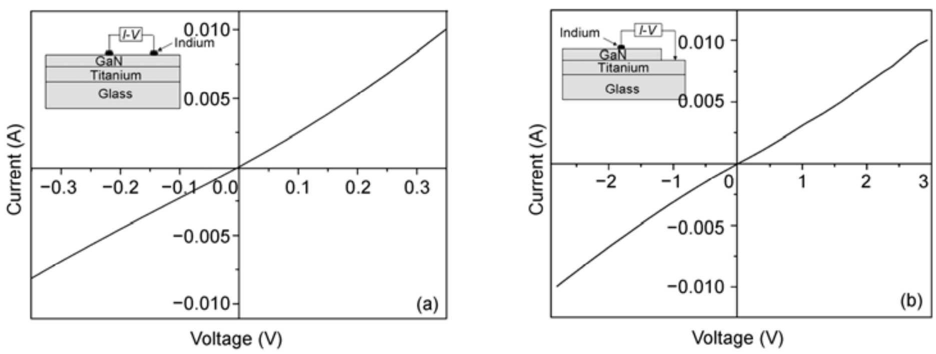

Figure 6 The test structure and *I-V* characteristics of indium/GaN film (a) and Ti/GaN film (b).

will benefit significantly from the proposed GaN/Ti structure.

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