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Thick AlN Epilayer Grown by Using the HVPE Method

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A thick AlN epilayer is grown directly on a c-plane sapphire substrate by using the hydride vapor phase epitaxy (HVPE) method with a small quantity of Al. The new type (RF + hot-wall) flow HVPE reactor used in the AlN epilayer growth is custommade. The growth temperatures of the source and the growth zones are set at 950 °C and 1145 °C, respectively. The characteristics of the AlN layer grown on a sapphire substrate are investigated by using energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectroscopy. The value of the full width at half maximum (FWHM) for the (002) peak from the AlN layer on the sapphire substrate is observed at 790 arcsec. From the small value of the FWHM, the AlN layer seems to be a well-arranged plane with a uniform (002) growth direction on a sapphire substrate.

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I. INTRODUCTION

Nitride research to further improve device performances and mitigate reliability issues is due to the immediate need for native nitride substrates. Though GaN substrates are commercially available, they are not suitable for high-Al-content AlGaN-based devices. Because AlN has a lattice constant close to that of GaN, a high thermal conductivity (3.2 W/cm K [1]), a high intrinsic electrical resistivity and a wide band gap (6.2 eV), it has been identified as a promising substrate material for ultraviolet (UV) light-emitting diodes (LED's) with high power, laser diodes (LD's), UV detectors and AlGaN/GaN high-frequency electronic devices (HEMT's) with ultra-high power [2–4]. Some groups reported the growth of high-quality bulk AlN by using the sublimation-recondensation method [5–7]. Bockowski, *et al.* [8] investigated a solution growth of AlN under a high nitrogen pressure. Although AlN crystals with low dislocation density can be grown by using these methods, the size and the shape of the AlN crystal prove to be rather difficult to control.

Another interesting approach to fabricating an AlN wafer is high-speed growth by using a hydride vapor phase epitaxy (HVPE) method. As opposed to AlN, some manufacturers have been producing GaN wafers of 2 inches in diameter by separating these thick HVPE GaN layers from starting substrates such as sapphire and GaAs [9–11]. Because the size and the shape of the grown layer depend on the kind of substrate, a HVPE method for the growth of a thick AlN epilayer is also worth investigating. However, investigations concerning the HVPE method for fabricating AlN epilayers have been limited [12–15].

As is well known, a thick AlN epilayer grown by using

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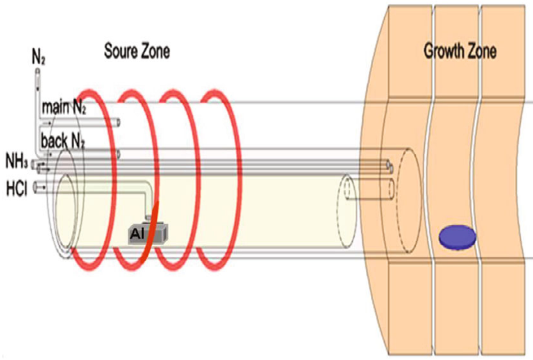

Fig. 1. (Color online) Schematic of the new type HVPE system.

the HVPE method is grown at a rapid growth rate and a high growth temperature, and AlN films grown at only a high growth rate deteriorate. Therefore, if an AlN bulk single crystal of high quality is to be obtained at a higher growth rate, the growth temperature must be increased. Because the migration of the chemical species adsorbed on the growth surface is promoted with increasing growth temperature and becomes the chemical species can be easily accommodated at an the appropriate site for epitaxial growth of AlN, the crystalline quality of the AlN epilayer grown at a high temperature is improved [16]. However, heating the substrate in a quartz reactor at a high temperature by using an electric furnace of the hot-wall type is impossible. Therefore, local heating of the substrate by using a heating susceptor is essential if a metal-organic vapor-phase epitaxy (MOVPE) method is to be used to grow an AlN epilayer at high temperature.

In this research, a thick AlN epilayer is grown directly on a c-plane sapphire substrate by using the HVPE method with a small amount of Al. The surface and the cross section of the AlN epilayer are observed by using scanning electron microscopy (SEM). The characteristics of the AlN layer grown on a sapphire substrate are investigated by using energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectroscopy.

II. EXPERIMENTS

A thick AlN epilayer is grown by using the HVPE method. A new, custommade (RF + hot-wall) flow HVPE reactor is used for the growth of the AlN epilayer Figure 1 shows a schematic of the HVPE system. The reactor with a RF-heating-type source zone and a hot-wall-type growth zone has two types of heat zones that are heated independently by using separate heater systems. Therefore, the cell filled with the source is composed of conductive graphite which can withstand high temperature. On the other hand, the growth zone is heated by using a hot-wall furnace. The reactor is composed of a graphite source boat, a quartz outer tube, an inner tube, a susceptor, a complicated liner and flow channels. The Al source is loaded into the source zone, and the weight of the Al source is about 7 g. Aluminum trichloride ($AlCl_3$) is formed in the source zone by reactions with the hydrogen-chloride (HCl) gas flowing over the aluminum metal a temperature of about 950 °C. Ammonia (NH3) gas flows through the growth zone. In our previous experiments, we obtained the optimum condition to grow the AlN epilayer by changing the growth temperature from 1100 °C to 1200 °C. The best results showed that the optimum temperature for growing an AlN epilayer in our HVPE was 1145 °C (data are not shown). The c-plane sapphire substrate is made parallel to the flow of the gas in the growth zone, which is at a temperature of about 1145 °C.

The AlN epilayer is grown directly on a 2-inch-diameter c-plane sapphire wafer. The growth is performed with a single growth step without the use of a nucleation layer, the growth step and substrate patterning. Uniform films are produced with a HCl gas flow of 100 sccm, a NH_3 gas flow of 2 slm, and a pressure of 760 Torr by using nitrogen as the carrier gas. The growth time of the AlN epilayer is 1 h. The XRD rocking curve is measured to determine the crystal's quality. The full width at half maximum (FWHM) values of the rocking curves are measured by using an omega scan of the (002) reflection and the (102) reflection in the symmetric and the skew symmetric geometrics, respectively. An additional characterization is performed by using SEM to measure the surface morphology and the thickness.

III. RESULTS AND DISCUSSION

The surface morphology and the thickness of the AlN epilayer grown directly on c-sapphire are observed by using SEM measurements. Figure 2 shows surface SEM images and EDS images of the AlN film grown by using the HVPE method at a high temperature. Figures 2(a) and (b) are surface SEM images measured at different positions in the AlN epilayer grown on 2-inch-diameter c-sapphire. Hexagonal-shaped grains are visible in Fig. 2. Figure 2(c) shows a surface SEM image of the AlN epilayer and the EDS results for the indicated area. From the EDS results in Fig. 2(c), the Al and the N elements, as well as impurities such as element of C and O, are shown.

Figure 3 shows cross-sectional SEM images of the AlN epilayer. Figures 3(a) and (b) show SEM images to investigate the uniformity of the thickness of the entire AlN epilayer and the exact thickness of the AlN epilayer, respectively. The thickness of the AlN epilayer is about 15.6 μm. The average growth rate of the AlN epilayer by using the HVPE method is about 0.26 μm/min (15.6 μm/h). During growth of the AlN epilayer, the amount of the Al source consumed is about 1.4 g. The

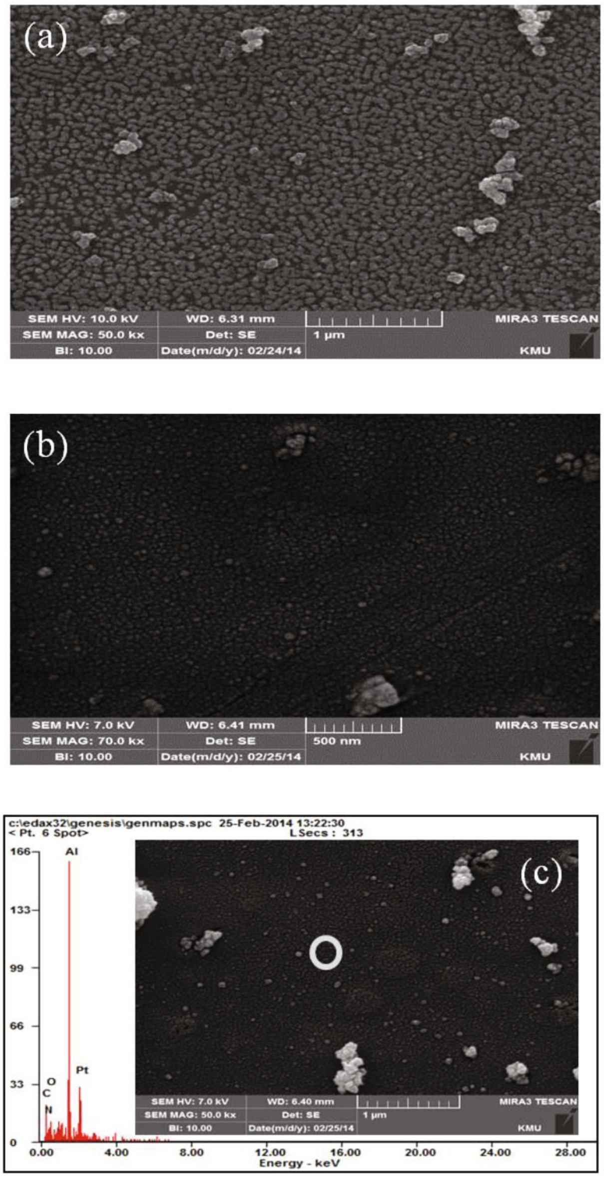

Fig. 2. (Color online) Surface SEM images of the AlN epilayer and the EDS result: (a), (b) Surface SEM images of the AlN epilayer and (c) EDS point scan result. The marked solid circle in (c) means the scan position for the EDS result.

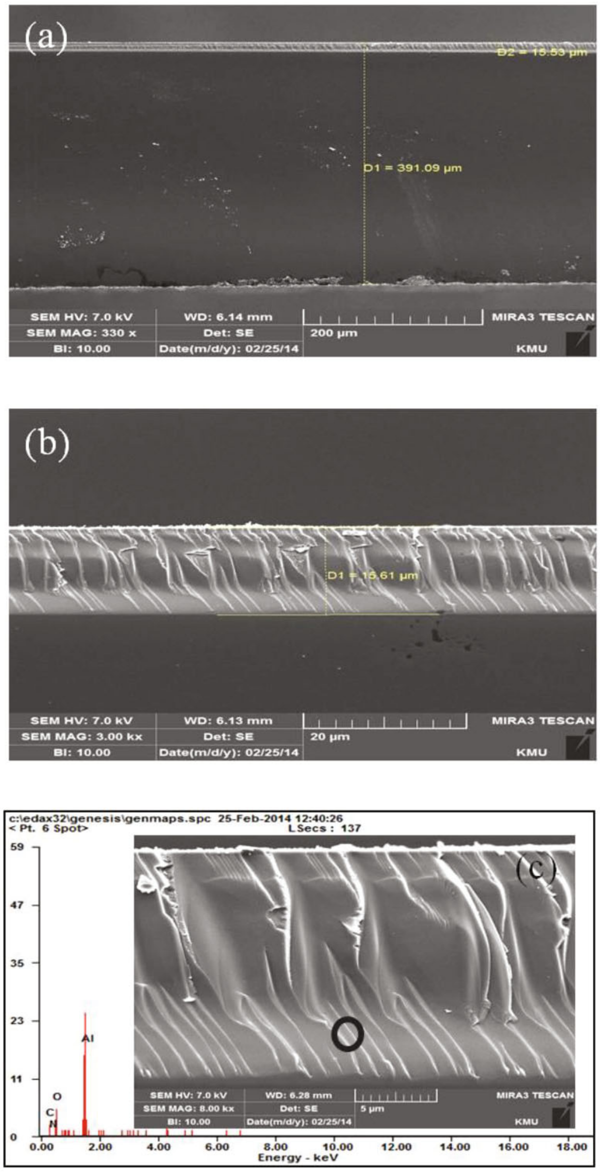

Fig. 3. (Color online) Cross-sectional SEM images of the AlN epilayer and the EDS result: (a), (b) cross-sectional SEM images of the AlN epilayer grown by using the HVPE method and (c) the EDS point scan result.

reaction rate between the HCl gas and the Al source is about 21.2%, which means that with our HVPE growth method, a thick AlN epilayer can be grown by using a small quantity of Al. Figure 3(c) shows an enlarged cross-sectional SEM image of the AlN epilayer and the EDS results from the indicated area. From the EDS results, elemental Al and N and impurities, such as elemental C and O, are seen.

Figure 4 shows the XRD results for the AlN epilayer. The X-ray diffraction employs a 2-theta/omega scan mode to examine the surface's crystalline quality. The AlN (002) and the AlN (004) peaks shown in Fig. 4(a) are observed at $2\theta = 36.1^\circ$ and $2\theta = 76.7^\circ$, respectively. The FWHM value of the AlN (002) peak is 790 arcsec. Several groups have demonstrated HVPE growth of AlN directly on sapphire substrates; the best XRD rocking curve FWHMs were in the ranges of 200 to 600 arcsec and 500 to 800 arcsec for on-axis and off-axis peaks, respectively [17–19]. The small value of the FWHM from these results means a well-arranged epilayer with a uniform growth direction. Figure 4(b) shows the rocking curves of ω scans for the (002) reflection of the AlN epilayer grown by using the HVPE method. For the ω scan, the FWHM value of the (002) reflection for calculating the density of screw threading dislocations (TDs) is about 0.17° [20]. The density of screw TDs (N_{screw}), is esti-

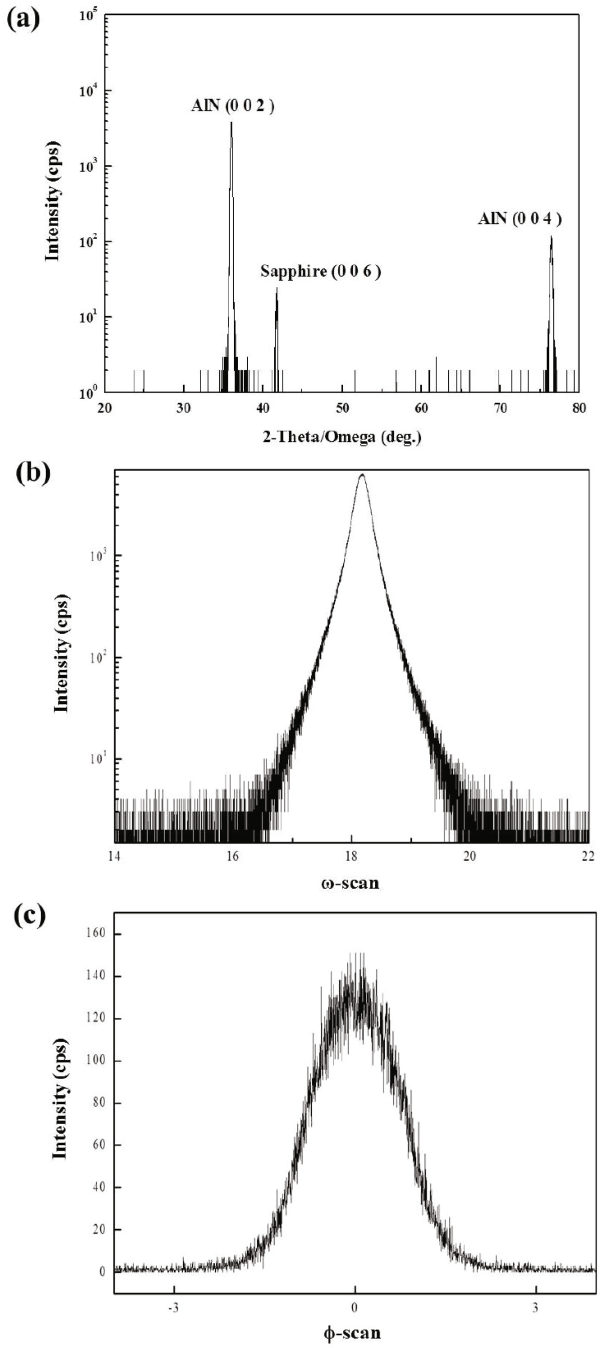

Fig. 4. (a) XRD intensity versus 2-theta/omega in the scan mode to examine the crystalline quality of the AlN epilayer. (b) XRD intensity versus omega in the scan mode to examine the crystalline quality of the AlN (002) epilayer. (c) XRD intensity versus ∅ in the scan mode to examine the crystalline quality of the AlN (102) epilayer.

mated by using the classical formula [21]. The value of N$_{screw}$ for the AlN film is estimated to be $\sim$1.91 $\times$ 10^9 cm^{-2}, which is large compared with the typical value for an AlN epilayer grown on sapphire. Figure 4(c) shows the rocking curves of the (102) reflection for the AlN epilayer grown by using the HVPE method. The figure shows the FWHM(ϕ) for the (102) lattice plane with respect to the c plane. The angle ϕ at the FWHM value for the rocking curve is estimated to be about 1.16°. The N$_{edge}$, the density of edge-type dislocations, is calculated to be $\sim$9.72 $\times$ 10^{10} cm^{-2}, which is about one order of magnitude higher than N$_{screw}$ in a 15.6-μm-thick AlN epilayer. The sharp decrease in the N$_{edge}$ value in the thick epilayer, as indicated by the FWHM value of the (102) rocking curve, could be due to increased termination of edge-type dislocations by forming loops with similar neighboring dislocations having opposite Burgers vectors with increasing epilayer thickness. The results indicate that the AlN epilayer acts as an effective dislocation filter [22]. With optimizations of the growth conditions and of the designs for the structures used in the HVPE method, the crystal quality of the AlN epilayer can be improved.

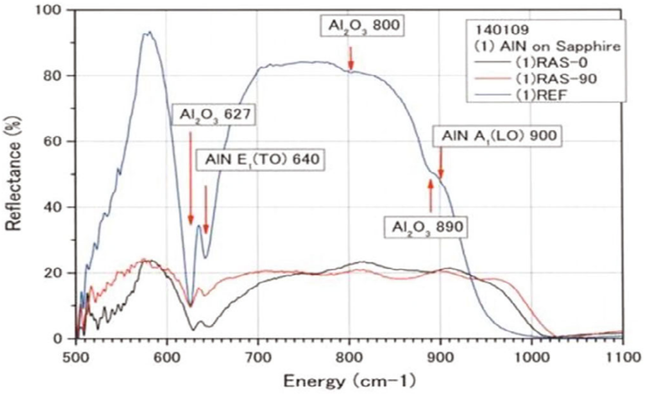

Fig. 5. (Color online) FTIR measurement results for the AlN epilayer.

Figure 5 shows the FTIR measurement results for the AlN epilayer. The FTIR measurement is used to investigate the characteristic frequency of the atoms constituting the material and having a characteristic vibration. The specific wavelength absorbed by the characteristic vibration has an energy corresponding to an infrared (IR) wavelength. Figure 5 shows the reflection ratio after IR scanning. The upper graph of the three in Fig. 5 is the FTIR-REF spectrum, and the other graphs in Fig. 5 are the FTIR-RAS spectra. The AlN E$_1$ and the AlN A$_1$ modes are observed at about 640 cm^{-1} and about 900 cm^{-1}, respectively. The A$_1$ and the E$_1$ peaks are located near the AlN longitudinal optical (LO) and the transverse optical (TO) phonon modes, respectively. The A$_1$ phonon modes in crystalline AlN appear in the range of 900 $\sim$ 950 cm^{-1} [23]. The measured frequencies from the FTIR-REF and the FTIR-RAS spectra are close to the characteristic frequency of the AlN epilayer.

As reported in a previous paper, AlN epilayers are generally grown at temperatures above 1200 °C because the crystalline quality is improved at higher growth temperatures. However, our growth temperature is 1145 °C, which is lower than the temperatures in other reports. Nevertheless, in our experimental results, the values from the FTIR spectra are in good agreement with the narrow FWHM value of the XRD result, which confirms the formation of crystalline AlN by using our HVPE method.

IV. CONCLUSION

A thick AlN epilayer is grown directly on a 2-inch-diameter c-plane sapphire substrate by using the HVPE method with a small quantity of Al. The thickness of the AlN epilayer is about 15.6 μm. During the growth of the AlN epilayer, the consumed quantity of Al is about 1.4 g. The XRD results show that the AlN (002) and the AlN (004) peaks are observed at $2\theta = 36.1^\circ$ and $2\theta = 76.7^\circ$, respectively. The measured values from the FTIR-REF and the FTIR-RAS spectra are both close to the characteristic frequency of the AlN crystal, respectively. From these results, an AlN epilayer seems to have been successfully grown on a sapphire substrate. We also expect to improve the luminous efficiency of wide-band gap devices based AlN epilayers with good crystalline quality by using our economical HVPE method.

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REFERENCES

[1] G. A. Slack, R. A. Tanzilli, R. O. Pohl and J. W. Vandersande, J. Phys. Chem. Solids **48**, 641 (1987).

[2] K. H. Kim, Y. S. Kim, S. H. Jeong, S. W. Jung and S. H. Lee, J. Korean Phys. Soc. **48**, 275 (2006).

[3] K. W. Nam, Y. K. Park, B. J. Ha, D. H. Shim and I. S. Song, J. Korean Phys. Soc. **47**, S309 (2005).

[4] J. K. Kim and S. H. Jeong, J. Korean Phys. Soc. **38**, 19 (2001).

[5] G. A. Slack and T. F. McNelly, J. Cryst. Growth **34**, 263 (1976).

[6] J. C. Rojo, G. A. Slack, K. Morgan, B. Raghothamachar, M. Dudley and L. J. Schowalter, J. Cryst. Growth **231**, 317 (2001).

[7] R. Schlesser, R. Dalmau and Z. Sitar, J. Cryst. Growth **241**, 416 (2002).

[8] M. Bockowski, M. Wroblewski, B. Łucznik and I. Grzegory, Mater. Sci. Semiconduct. Proc. **4**, 543 (2001).

[9] M. K. Kelly, R. P. Vaudo, V. M. Phanse, L. Gorgens, O. Ambacher and M. Stutzmann, Jpn. J. Appl. Phys. **38**, L217 (1999).

[10] S. S. Park, I. W. Park and S. H. Choh, Jpn. J. Appl. Phys. **39**, L1141 (2000).

[11] K. Motoki *et al.*, Jpn. J. Appl. Phys. **40**, L140 (2001).

[12] A. Nikolaev, I. Nikitina, A. Zubrilov, M. Mynbaeva, Y. Melnik and V. Dmitriev, Mater. Res. Soc. Symp. Proc. **595**, 5 (2000).

[13] Y. Melnik, D. Tsvetkov, A. Pechnikov, I. Nikitina, N. Kuznetsov and V. Dmitriev, Phys. Status Solidi A **188**, 463 (2001).

[14] O. Y. Ledyaev, A. E. Cherenkov, A. E. Nikolaev, I. P. Nikitina, N. I. Kuznetsov, M. S. Dunaevski, A. N. Titkov and V. A. Dmitriev, Phys. Status Solidi C **0**, 474 (2002).

[15] Y. Kumagai, T. Yamane, T. Miyaji, H. Murakami, Y. Kangawa and A. Koukitu, Phys. Status Solidi C **0**, 2498 (2003).

[16] Y. Kumagai, T. Yamane and A. Koukitu, J. Cryst. Growth **281**, 62 (2005).

[17] D. Kamber, Y. Wu, B. Haskell, S. Newman, S. DenBaars, J. Speck and S. Nakamura, J. Cryst. Growth **297**, 321 (2006).

[18] V. Soukhoveev, A. Volkova, V. Ivantsov, O. Kovalenkov, A. Syrkin and A. Usikov, Phys. Status Solidi C **6**, S333 (2009).

[19] J. Tajima, R. Togashi, H. Murakami, Y. Kumagai, K. Takada and A. Koukitu, Phys. Status Solidi C **8**, 2028 (2011).

[20] S. R. Lee, A. M. West, A. A. Allerman, K. E. Waldrip, D. M. Follstaedt, P. P. Provencio, D. D. Koleske and C. R. Abernathy, Appl. Phys. Lett. **86**, 241904 (2005).

[21] C. G. Dunn and E. F. Koch, Acta Metall. **5**, 548 (1957).

[22] B. N. Pantha, R. Dahal, M. L. Nakarmi, N. Nepal, J. Li, J. Y. Lin, H. X. Jiang, Q. S. Paduano and D. Weyburne, Appl. Phys. Lett. **90**, 241101 (2007).

[23] G. V. Tendeloo, K. T. Faber and G. Thomas, J. Mater. Sci. **18**, 525 (1983).