Pergamon

Materials Research Bulletin 35 (2000) 125–133

Materials Research Bulletin

Transmission electron microscopic study of GaAs/Ge heterostructures grown by low-pressure metal organic vapor phase epitaxy

Mantu Kumar Hudait[a,b,1], S.B. Krupanidhi[a,*]

[a]*Materials Research Centre, Indian Institute of Science, Bangalore 560 012, India*
[b]*Central Research Laboratory, Bharat Electronics, Bangalore 560 012, India*

(Communicated by C.N.R. Rao)
Received 27 February 1999; accepted 5 March 1999

Abstract

GaAs/Ge heterostructures were grown under different growth conditions by low-pressure metal organic vapor phase epitaxy (LP-MOVPE) and investigated by transmission electron microscopy (TEM). Abrupt heterointerface and antiphase domain (APD)-free single domain GaAs epilayers on Ge substrates were achieved under specific growth conditions. The lattice indexing of high-resolution transmission electron microscopy (HRTEM) exhibited excellent lattice line matching between the GaAs epilayer and the Ge substrate. These results led us to conclude that the optimal growth parameters for achieving high-quality GaAs/Ge heterostructure are As/Ga ratio of ~88:1, growth rate of ~3 μm/h, and growth temperature of 675°C.

Keywords: A. Thin films; A. Semiconductors; B. Epitaxial growth; C. Electron microscopy; D. Defects

* Corresponding author. Tel.: +91-80-3311330; fax: +91-80-334-1683.

E-mail addresses: sbk@mrc.iisc.ernet.in (S.B. Krupanidhi), hudait@ee.eng.ohio-state.edu or hudait.1@osu.edu (M.K. Hudait).

[1] Present address: Postdoctoral Researcher, Electronic Materials & Photovoltaic Lab, Department of Engineering, Ohio State University, 2015 Neil Avenue, Columbus, OH 43210-1272. Tel.: 614-292-1721; fax: 614-292-9562.

PII: PII S0025-5408(00)00191-4

1. Introduction

The nearly lattice matched GaAs/Ge (0.07%) heterostructures have received much attention as starting materials for space quality solar cell applications. This is mainly because they can replace conventional GaAs/GaAs cells, which are expensive and suffer from fragility [1–7]. Due to its high mechanical strength, Ge is an optimized substrate material in terms of its power-to-weight ratio for high efficiency GaAs/Ge solar cells. Such cells are now replacing Si solar cells in some satellite applications [8–10]. As large-area, minority-carrier devices, III-V/Ge cells are extremely sensitive to defects. The elimination of antiphase domains (APDs), which are characteristics of the polar-on-nonpolar epitaxy, and suppression of large-scale interdiffusion across the GaAs/Ge heterointerface remain key challenges to achieving increased yield, reliability, and performance.

The low lattice mismatch of the GaAs/Ge system suggests that it should be nearly dislocation free. The polar-on-nonpolar heteroepitaxy poses several unique problems of its own, namely, the lattice and thermal expansion coefficient mismatch between GaAs and Ge, leading to misfit dislocations (MDs); the difference in lattice symmetry between the III-V compound and the Ge substrate, which creates APDs bounded by antiphase boundary (APB) in the III-V epilayer; and the interdiffusion of Ga, As, and Ge across the heterointerface [11–21]. GaAs can be grown epitaxially on Ge in two equivalent orientations corresponding to an exchange of Ga and As sublattices [11], which often leads to the formation of APDs. An APB separates domains of different orientations. Since GaAs is a polar material, the APBs act as nonradiative recombination surfaces [11,22]. Thus, to grow device-quality single-domain GaAs/Ge, careful control of the substrate surface structure [23] and the initial growth conditions [13–15,24] is essential. The self-annihilation of APDs could lead to single domain epitaxy of polar materials on nonpolar materials [15]. In such a case, however, there are still APBs in the epilayer up to a certain region from the interface into the epilayer, which could be harmful to devices based on the heterointerface properties.

In recent years, there have been several reports aimed at understanding the growth mechanisms and interfacial properties of GaAs/Ge heterojunction, APDs [13,14,18,22], interdiffusion [19,20,25], and band discontinuities [26]. Several authors [12–15,18,24] have used the misorientation of Ge substrates, in order to grow APD-free GaAs on Ge by metal organic vapor phase epitaxy (MOVPE). There is no unique rule for selection of off-orientation of the Ge substrates and the initial growth conditions, such as growth temperature, V/III ratio, and the growth rate that should be used for single-domain GaAs/Ge grown by MOVPE. The structure of offcut (100) Ge surface is also highly sensitive to the conditions of GaAs growth initiation. Varying degrees of success in GaAs/Ge heteroepitaxy by MOVPE and closed-space vapor transport (CSVT) have been reported [13,14,17,27,28]. Overall, it should be expected that the ability to grow APD-free GaAs/Ge depends highly on the inherent chemistry of the particular growth technique. The best MOVPE GaAs/Ge heterostructure [13,14] has been grown by using initial arsine (AsH_3) exposure. To avoid the formation of APDs, which are harmful to solar cell performance because they reduce the short circuit current, off-oriented substrates were used in this investigation. A further optimization of the GaAs growth conditions on Ge substrate is needed for the reduction of the element interdiffusion across the GaAs/Ge interface. Suppression of APDs is the major challenge in the realization of the device-quality GaAs/Ge structure. The efforts dedicated to solving these problems have allowed higher conversion efficiencies in AMO on large area substrates by low-pressure (LP)-MOVPE.

The aim of this paper is to report the main results of a careful investigation of the crystal quality of GaAs/Ge single heterostructure by conventional transmission electron microscopy (CTEM). High-resolution TEM (HRTEM) was carried out to characterize the interface quality and the nature of the defects.

2. Experimental

GaAs/Ge heterostructures were grown by LP-MOVPE. High-quality Sb-doped n^+-Ge substrates 2°, 6°, and 9° off (100) towards [110] direction were used as substrates in each MOVPE growth run. From previous characterizations of the epitaxial GaAs layers on these three off-oriented Ge substrates, e.g., Si incorporation in GaAs by low temperature photoluminescence (LTPL) spectroscopy [24] and surface morphology by atomic force microscopy [29], we found that 6° off-oriented Ge substrate was better than 2° and 9° Ge substrates. We report here only the 6° offset results under close observation of heterointerface, because such a substrate miscut gave the best results [24,29]. It has been reported [30] to be effective in reducing the formation of APDs, which may be generated at the interface between a polar semiconductor and a nonpolar one.

The source materials were trimethylgallium (TMGa), 100% arsine (AsH_3), and palladium purified H_2 as the carrier gas. During growth, the pressure inside the reactor was kept at 100 Torr and the growth temperature was varied from 600 to 700°C. The TMGa and AsH_3 fluxes were adjusted so that a growth rate ranging from 3 to 12 μm/h was obtained. The total flow rate was 2 SLPM. The thickness of the epitaxial layers investigated ranged from about 1.5 to 6.5 μm.

The epitaxial GaAs/Ge heterointerfaces were prepared by Ar^+ ion thinning for cross-sectional observations. The CTEM investigations were performed using a Hitachi H-9000 UHR ultra-high resolution electron microscope operated at 300 kV.

3. Results and discussion

The epitaxial films were investigated using TEM to reveal the characteristics of misfit dislocations (MDs) and other crystalline defects. In general, the dominant crystalline defects observed in the GaAs epi-film grown on Ge are APDs and dislocations. Fig. 1 shows the cross-sectional HRTEM image of GaAs on Ge substrates, using an As prelayer, a growth temperature of 700°C, a V/III ratio of 88.20, and a growth rate of ~3 μm/h. Close observation of the interface area in Fig. 1 reveals many threading dislocation groups and very few APDs at the heterointerface, as observed by several authors [14,18,31–33]. APDs should not be observed in the layer, because of the miscutting of the substrate [12,30,34]. The presence of APDs at the heterointerface may be due to the high growth temperature or low growth rate.

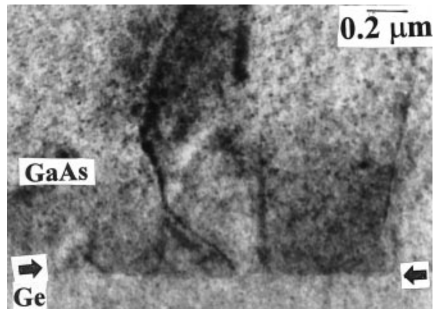

Fig. 1. [110] TEM cross-sectional micrograph of GaAs layers grown at 700°C with a growth rate of 3 μm/h and V/III ratio of 88.20.

Fig. 2 shows a TEM cross-section micrograph of GaAs/Ge grown at 700°C, with a V/III ratio of 29.40 and growth rate of 12 μm/h. From Fig. 2, it is seen that the interface between the GaAs epilayer and the Ge substrate is not sharp. In addition to MDs, other features are observed, as reported by several authors [30,32]. These special patterns are attributed to APDs. With a decrease in V/III ratio, we observe that APDs are present along the interface.

Franzosi et al. [32] observed that the epilayer crystal quality is strongly affected by the growth rate: layers grown at low growth rate (1 μm/h) exhibit planar defects that are not present in films grown at high deposition rates (10 μm/h). It has recently been argued [35,36] that lattice mismatch plays a minor role in the formation of planar defects such as twins or stacking faults, which probably originate during the early stages of the epitaxial growth. These defects may propagate from the interface to the top of the layer. Generally, MDs are seen at the heterointerface if the film thickness is greater than the critical thickness (290 nm $< t_c <$ 450 nm) [19]. Suzuki et al. [37] reported an enhancement of the formation of APDs at low V/III ratio for GaP on Si, which they ascribed to three-dimensional growth at low V/III ratio. For a certain growth rate, a higher V/III ratio would result from substrates being preheated at a higher AsH_3 partial pressure before growth starts. Li et al. [14] pointed out that the V/III ratio may influence the surface composition of the substrates, which in turn affects the nucleation of GaAs on Ge substrate. They also mentioned that high AsH_3 partial pressure might influence the growth of the nuclei into clusters that coalesce with each other.

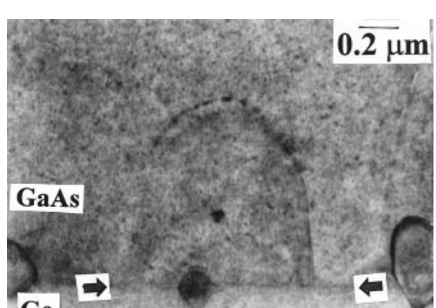

Fig. 2. [110] TEM cross-sectional micrograph of GaAs layers grown at 700°C with a growth rate of 12 μm/h and V/III ratio of 29.40.

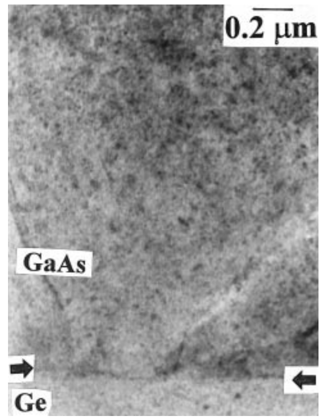

Fig. 3. [110] TEM cross-sectional micrograph of GaAs layers grown at 675°C with a growth rate of 3 μm/h and V/III ratio of 88.20.

At the critical AsH_3 pressure, both As and Ga can be incorporated in the same steps so that the formation of APDs occurs. Another mechanism proposed by Li et al. [14] is that a relatively high pressure of AsH_3 is required to lock the phase of the GaAs nuclei formed at the steps before they are connected to each other. In order to have APD-free GaAs on Ge, a high V/III ratio and relatively low growth temperature may be needed.

Fig. 3 shows the TEM cross-sectional image of GaAs on Ge at V/III ratio of 88.20, 3 μm/h growth rate, and growth temperature of 675°C. It can be seen that for the layer grown under these conditions, the interface between the GaAs epilayer and the Ge substrate was very sharp; no APDs were observed at the heterointerface. The morphology of the GaAs layer was very good and the electrochemical capacitance voltage (ECV) profile of Si-doped GaAs on Ge showed a very sharp interface [24]. Nucleation of GaAs directly on the Ge surface (without any epitaxial Ge growth) typically resulted in high defect densities due to the uncontrolled initial surface.

Ringel et al. [31] found that a Ge epitaxial film annealed above 640°C for ~20 min, coupled with a large 6° offcut, results in double-stepped Ge surfaces, which greatly suppress APD formation [30]. They observed that growth on Ge surfaces that were not sufficiently annealed typically showed high APD densities. The substrate temperature during the initial 100 nm GaAs growth is critical. Growth at too low a temperature results in excess As point defects, which nucleate dislocation loops. These loops expand during the subsequent high temperature GaAs growth to generate high threading dislocation densities in the thick GaAs film [18]. On the other hand, the growth at higher temperatures and low growth rates may result in the formation of unwanted p-n junctions due to simultaneous indiffusion of Ga and As inside the Ge substrate. This in turn reduces the solar cell efficiency [5]. The transition of APD-free → APDs → APD-free film with increasing growth temperature has been found [38] experimentally by Fischer et al. in molecular beam epitaxy (MBE)-grown GaAs on Si. Li et al. [14] pointed out that such a transition temperature will depend on other parameters, such as the substrate misorientation angle and the growth rate, in the MOVPE growth of GaAs on Ge substrates. From our cross-sectional TEM observations of the GaAs/Ge

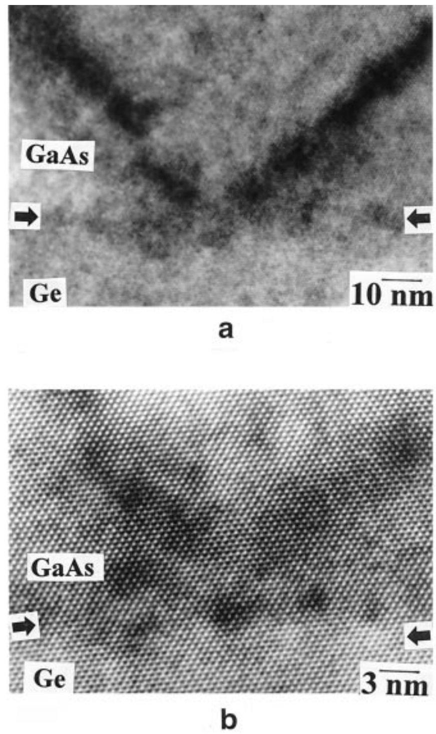

Fig. 4. (a) [110] cross-sectional HRTEM image of the heterointerface of GaAs/(100) Ge heterostructures grown by LP-MOVPE; (b) high magnification image of a portion of the TEM image shown in (a).

heterointerface, we conclude that a growth temperature of ~675°C, V/III ratio of ~88:1, and growth rate of ~3 μm/h in the LP-MOVPE process is the optimal growth condition for APD-free GaAs on 6° offcut Ge substrate.

The heterointerface between the GaAs epilayer and Ge substrate was evaluated at atomic scale. Fig. 4(a) shows a typical (110) cross-sectional low magnification HRTEM image of the sample grown at 675°C, V/III ratio of 88.20, and growth rate of 3 μm/h. It can be seen from this figure that the GaAs/Ge interface is extremely abrupt and there are some V-shaped defects at the heterointerface. A V-shaped defect was observed by Timò et al. [39] in the LP-MOVPE growth of GaAs/Ge under a particular AsH_3 partial pressure. In the V-shaped defect, holes were observed at the end of the two sides of the defect. This characteristic of the V-shaped defect is very harmful for solar cell devices. During the metallization process, some metal particles can enter these holes, resulting in leakage across the p-n junction.

In order to check the lattice plane of the V-shaped defects, a high magnification HRTEM image (Fig. 4b) was taken of a portion of Fig. 4a. From Fig. 4b, it is seen that there is no atomic step and, hence, no V-shaped defects, which were expected to be present. The heterointerface is observed to be extremely sharp. The epitaxial growth of GaAs and Ge substrate is clearly visible in the high-resolution image shown in Fig. 4b, with the well-resolved GaAs lattice lines extending all the way down to the Ge surface closely matching with the Ge lattice. Further, the heterointerface boundary region does not show any extra

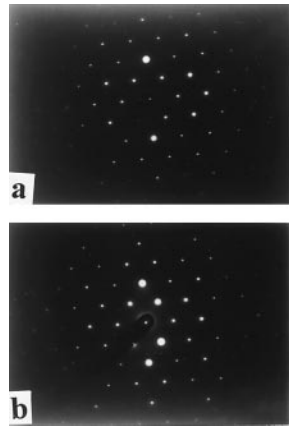

Fig. 5. Selective area electron diffraction patterns for (a) epi-GaAs film and (b) (100) Ge substrate.

lines due to MDs, which was observed by Franzosi et al. [32]. The strong spots in the selected area electron diffraction (SAED) pattern of the film and the substrate, shown in Fig. 5a and b, respectively, indicate single crystal. It was observed by lattice indexing that MOVPE growth layers of GaAs under present growth conditions exhibit epitaxial growth in the (100) direction normal to the substrate surface. Figs. 6 and 7 show the high magnification cross-sectional HRTEM images of samples grown under different growth conditions. It can be seen that under all of the growth conditions, the GaAs lattice lines extended down to the Ge surfaces. There is no lattice line discontinuity between the GaAs epilayer and Ge substrate due to the MDs.

4. Conclusions

GaAs/Ge heterostructures have been grown by LP-MOVPE and investigated by cross-sectional HRTEM. We have identified the MOVPE growth parameters (i.e., growth temperature, ~675°C; V/III ratio, ~88:1; growth rate, ~3 μm/h) that minimize antiphase domains

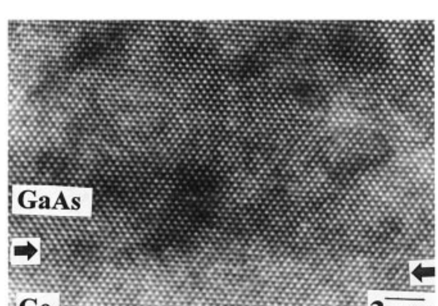

Fig. 6. [110] cross-sectional HRTEM image of heterointerface of GaAs/(100) Ge heterostructures grown at 700°C with a growth rate of 3 μm/h and V/III ratio of 88.20.

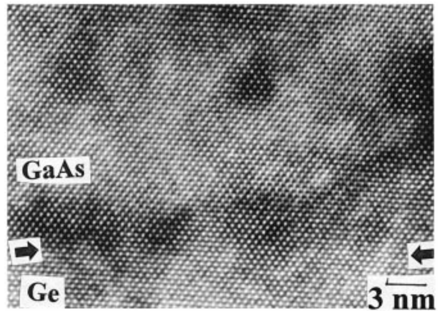

Fig. 7. [110] cross-sectional HRTEM image of heterointerface of GaAs/(100) Ge heterostructures grown at 700°C with a growth rate of 12 μm/h and V/III ratio of 29.40.

and prevent unexpected misfit dislocation densities based on our study of the GaAs/Ge heterointerface. The lattice indexing of HRTEM exhibited an excellent lattice line matching between GaAs epilayer and Ge substrate. The heterointerface was found to be extremely abrupt in a specific growth condition. Growth along (100) direction was confirmed by HRTEM selective area diffraction pattern. The elimination of APDs and the suppression of interdiffusion are a consequence of atomic scale control of the GaAs/Ge heterointerface. This is an encouraging step towards the development of space-quality solar cells.

References

[1] R.A. Metzger, Compound Semicond 2 (1996) 25.
[2] M. Kato, K. Mitsui, K. Mizuguchi, N. Hayafuji, S. Ochi, Y. Yukimoto, T.Murotani, K. Fujikawa, Proc 18th IEEE Photovolt Spec Conf (1985) 14.
[3] C. Flores, B. Bollani, R. Campesato, F. Paletta, D. Passoni, G. Timò, A. Tosoni, Solar Energy Mater 23 (1991) 356.
[4] K.I. Chang, Y.C.M. Yeh, P.A. Iles, J.M. Tracy, R.K. Morris, Proc 19th IEEE Photovolt Spec Conf (1987) 273.
[5] P. A. Iles, Y. C. M. Yeh, F. H. Ho, C. L. Chu, C. Cheng, IEEE Electron Device Lett EDL-11 (1990) 140.
[6] T. Whitaker, Compound Semicond 4 (1998) 32.
[7] J.C. Chen, M.L. Ristow, J.I. Cubbage, J.G. Werthen, J Electron Mater 21 (1992) 347.
[8] M. Meyer, R. A. Metzger, Compound Semicond 2 (1996) 22.
[9] C. Flores, B. Bollani, R. Campensato, D. Passoni, G. L. Timò, Microelectron Eng 18 (1992) 175.
[10] S.J. Wojtczuk, S.P. Tobin, C.J. Keavney, C. Bajgar, M.M. Sanfacon, L.M. Geoffroy, T.M. Dixon, S.M. Vernon, J.D. Scofield, D.S. Ruby, IEEE Trans Electron Devices ED-37 (1990) 455.
[11] H. Kroemer, J Cryst Growth 81 (1987) 193.
[12] P.R. Pukite, P.I. Cohen, J Cryst Growth 81 (1987) 214.
[13] Y. Li, L. Lazzarini, L.J. Giling, G. Salviati, J Appl Phys 76 (1994) 5748.
[14] Y. Li, G. Salviati, M.M.G. Bongers, L. Lazzarini, L. Nasi, L.J. Giling, J Cryst Growth 163 (1996) 195.
[15] Y. Li, L.J. Giling, J Cryst Growth 163 (1996) 203.
[16] K. Morizane, J Cryst Growth 38 (1977) 249.
[17] L. Lazzarini, Y. Li, P. Franzosi, L.J. Giling, L. Nasi, F. Longo, M. Urchulutegui, G. Salviati, Mater Sci Eng B 28 (1994) 502.
[18] S.M. Ting, E.A. Fitzgerald, R.M. Sieg, S.A. Ringel, J Electron Mater 27 (1998) 451.

[19] G. Timò, C. Flores, B. Bollani, D. Passoni, C. Bocchi, P. Franzosi, L. Lazzarini, G. Salviati, J Cryst Growth 125 (1992) 440.
[20] S.J. Wojtczuk, S.P. Tobin, M.M. Sanfacon, V.E. Haven, L.M. Geoffroy, S.M. Vernon, Proc 22nd IEEE Photovolt Spec Conf (1991) 73.
[21] Y.C.M. Yeh, K.I. Chang, C.H. Cheng, F. Ho, P. Iles, Proc 20th IEEE Photovolt Spec Conf (1988) 451.
[22] P.M. Petroff, J Vac Sci Technol B 4 (1986) 874.
[23] J.M. Olson, W.E. McMahon, Paper presented at the 2nd World Conference on Photovoltaic Solar Energy Conversion, Vienna, Austria, 6–10 July 1998 (NREL/CP-520-25045).
[24] M.K. Hudait, S.B. Krupanidhi, submitted to J Electron Mater.
[25] N. Chand, J. Klem, T. Henderson, H. Morkoç, J Appl Phys 59 (1986) 3601.
[26] R.S. Bauer, H.W. Sang Jr., Surface Science 132 (1983) 479.
[27] N. Guelton, R.G. Saint-Jacques, G. Lalande, J-P. Dodelet, J Mater Res 10 (1995) 843.
[28] G. Lalande, N. Guelton, D. Cossement, R.G. Saint-Jacques, J-P. Dodelet, Can J Phys 72 (1994) 225.
[29] M.K. Hudait, S.B. Krupanidhi, Mater Res Bull 35 (6) (2000) (in press, EO#1638).
[30] S. Strite, M.S. Unlu, K. Adomi, G.B. Gao, A. Agarwal, A. Rockett, H. Morkoç, D. Li, Y. Nakamura, N. Otsuka, J Vac Sci Technol B 8 (1990) 1131.
[31] S.A. Ringel, R.M. Sieg, S.M. Ting, E. A. Fitzgerald, Proc 26th IEEE Photovolt Spec Conf (1997) 793.
[32] P. Franzosi, L. Lazzarini, G. Salviati, M. Scafferdi, G. Timò, Inst Phys Conf Ser 117 (1991) 399.
[33] J.M. Kuo, E.A. Fitzgerald, Y.H. Xie, P.J. Silverman, J Vac Sci Technol B 11 (1993) 857.
[34] K. Mizuguchi, N. Hayafuji, S. Ochi, T. Murotani, K. Fujikawa, J Cryst Growth 77 (1986) 509.
[35] F. Ernst, P. Pirouz, J Appl Phys 64 (1987) 4526.
[36] J.W. Lee, H.L. Tsoi, J Vac Sci Technol B 5 (1987) 819.
[37] T. Suzuki, T. Soga, T. Jimbo, and M. Umeno, J Cryst Growth 115 (1991) 158.
[38] R. Fischer, H. Morkoç, D.A. Neuman, H. Zabel, C. Choi, N. Otsuka, M. Longerbone, L.P. Erickson, J Appl Phys 60 (1986) 640.
[39] G.L. Timò, C. Flores, R. Campesato, D. Passoni, B. Bollani, Mater Sci Forum 203 (1996) 97.