A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 52 2007 Issue 4

A. VLASOV*, O. BONCHYK**, I. FODCHUK***, R. ZAPLITNYY ***, A. BARCZ****, Z. ŚWIĄTEK*****, L. LITYŃSKA-DOBRZYŃSKA*****, P. ZIĘBA*****, E. BIELAŃSKA*****, J. GUŚPIEL*****

THE CONTROLLED DOPING AND STRUCTURAL HOMOGENEITY OF CdHgTe EPITAXIAL LAYERS

KONTROLOWANE DOMIESZKOWANIE I JEDNORODNOŚĆ STRUKTURALNA WARSTW EPITAKSJALNYCH CdHgTe

X-ray diffraction methods as well as atomic force microscopy (AFM) and secondary ion mass spectroscopy (SIMS) were used to study the controlled doping and structural homogeneity of HgCdTe epitaxial layers. The investigated layers were obtained by the evaporation-condensation-diffusion (ECD) method in the process of isothermal growth. Two types of substrates for CdHgTe ECD growth were used: (110) and (111) CdTe monocrystals with As ion implanted surface layer at a dose of $1{\times}10^{15}cm^{-2}$ and an energy of 100 keV. Structural changes in damaged areas of CdTe crystals that arise at the ion beam implantation and the influence of radiation defects on the quality of obtained layers are analyzed.

Keywords: doping, ion implantation, epitaxial layers, CdHgTe

W badaniach kontrolowanego domieszkowania i jednorodności strukturalnej warstw epitaksjalnych CdHgTe wykorzystano metody dyfrakcji rentgenowskiej oraz mikroskopię sił atomowych i spektroskopię masową jonów wtórnych. Warstwy otrzymano metodą parowanie – kondensacja – dyfuzja w procesie wzrostu izotermicznego. Wykorzystano dwa typy podłoża: monokryształy CdTe o orientacji (110) i (111) poddane implantacji jonowej As o dozie $1{\times}10^{15}cm^{-2}$ i energii 100 keV. Przeprowadzono analizę zmian strukturalnych w uszkodzonych obszarach kryształów CdTe wywołanych przez implantację jonową oraz wpływu defektów radiacyjnych na jakość otrzymanych warstw.

1. Introduction

Cadmium telluride is the most suitable material for epitaxial growth of CdHgTe narrow-gap epitaxial solid solutions which are being widely used for fabrication of high efficient IR detectors [1]. The ion implantation of impurities into undoped CdTe substrates is used for the epitaxial growth of doped CdHgTe layers by the evaporation-condensation-diffusion (ECD) modification of the isothermal vapour phase epitaxy (ISOVPE) method [2]. The real crystal structure of substrate surface, particularly its defective state, has significant importance during the initial stages of epitaxial growth. Most of the physicochemical processes which are responsible for absorption, interdiffusion of the main components and diffusion of doping impurity during the process of ECD epitaxy of CdHgTe strongly depend on the defective state of the substrate surface. The application of ion implantation as an efficient source of impurity requires maximum of information concerning the set of defects on the substrate surfaces after ion incorporation, as well as influence of radiation defects on the dopant diffusion process and the quality of obtained layers. The attention of authors is focused on the study of formation of the imperfect surface layers in the CdTe crystals during the As ion implantation and on the influence of these layers on the growth of As doped CdHgTe epitaxial layers.

2. Experiment

In order to study the influence of defective layer created on the surface of CdTe substrates immediately after ion implantation on the ECD epitaxial growth process, we have conducted complex research of both, substrates

* NATIONAL UNIVERSITY, 50 DRAGOMANOV STR., 79005 LVIV, UKRAINE
** INSTITUTE FOR APPLIED PROBLEMS OF MECHANICS AND MATHEMATICS OF NASU, 3-B NAUKOVA STR., 79601, LVIV, UKRAINE
*** CHERNIVTSI FEDKOVICH NATIONAL UNIVERSITY, 19 UNIVERSITETSKA STR., 74012, CHERNIVTSI, UKRAINE
**** INSTITUTE OF PHYSICS OF POLISH ACADEMY OF SCIENCES, 02-668 WARSAW, 32/46 AL. LOTNIKOW, POLAND
***** INSTITUTE OF METALLURGY AND MATERIALS SCIENCE, POLISH ACADEMY OF SCIENCES, 30-059 CRACOV, 25 REYMONTA STR., POLAND

with ion-implanted surface and doped epitaxial layers grown on them.

Undoped oriented monocrystals of CdTe grown by Bridgemann method with a dislocation density of ~$5\cdot10^4$ cm^{-2} were used as test subjects during the experiments. These crystals are being used as substrates for the ECD growth of CdHgTe epitaxial layers [3]. Flatness and mirror-like surfaces of CdTe substrates were achieved by means of an abrasive-free chemico-mechanical polishing in a bromine-butanol etchant. Impurity sources on the surfaces of these substrates were created by As implantation. Implantations have been carried out on "Balzers" MPB-202 ion-beam device. In all experiments the As atoms were implanted with the energy E = 100 keV and the dose $D = 1\times10^{15}$ cm^{-2}. The ISOVPE growths of the investigated CdHgTe epitaxial layers were performed in closed system using identical technological regimes. The scheme of solid-state doping process during ECD epitaxy of CdHgTe is shown in Fig. 1. The growth system is composed of parallel source (HgTe) and substrate (CdTe) with the interspace filled with ambient vapour (Hg and Te_2). The driving force for the transport is the difference in the equilibrium pressures of Te_2 vapour over the HgTe crystal and CdHgTe substrate. Here x_s denotes surface composition, z_s – thickness of the deposited layer CdHgTe, d – size of the spacing, with d being approximately by two orders of magnitude larger than z_s. The temperature of epitaxial CdHgTe growth was equal to 600°C. In order to increase the number of mercury vacancies created at the final stage of CdHgTe epitaxy, an annealing in the isothermal regime in mercury vapour at the temperature of 320°C was carried out. Undoped epitaxial layers of CdHgTe had n-type conductivity at these regimes of growth and post-growth annealing.

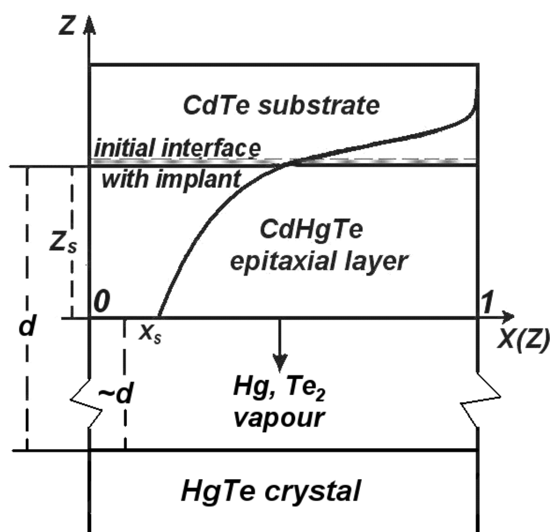

Fig. 1. ISOVPE geometry for the growth of variable gap epitaxial layer of HgCdTe

For analysis of the structural changes in the surface layers we used the single-crystal topography scheme and the scheme of double-crystal spectrometer (n, -n), with asymmetric and skew-asymmetric geometry of X-ray diffraction. For the qualitative analysis of changes taking place in the surface layers the method based on Fourier analysis of the curves of diffracted reflection was used.

The distribution of impurity concentration and the profiles of composition of CdHgTe epitaxial layers were determined by the Secondary Ion Mass Spectroscopy (SIMS) using Cameca IMS-6F device. The surface morphology of samples was investigated by noncontact atomic force microscopy (AFM).

The electrical transport properties of CdHgTe samples (concentration of main charge carriers ($|N_A - N_D|$) and their mobility (μ_H) were determined by the standard Hall measurements at $T = 77K$ and the magnetic fields ranging from 0.005 to 1.7 T. The surface composition (x_s) of variable band-gap epitaxial CdHgTe layers was determined by means of optical absorption.

3. Results and discussion

In the first series of experiments the CdTe (111) single crystal was used as an object of the investigation. This research direction was chosen due to the fact that during the impurity implantation into the compactly packed crystal surface with sphalerite structure the ion channeling effect does not influence the doping and the role of radiation defects rises accordingly [4].

3.1. Analysis of the implanted surface of CdTe

After the preparatory work half of the sample surface (CdTe monocrystal wafer) was covered by a mask. On completing the implantation process the mask was removed from the sample, afterwards the sample was split in few parts in order to conduct AFM and X-ray structural investigations. The depth of As penetration in the implanted part of the crystal both after the implantation and diffusion treatment in Cd vapour at T = 600°C during 10 minutes was determined by SIMS analysis. Such thermal and time regimes of the above mentioned annealing were chosen with the aim that the diffusion experiment could be conducted on the CdTe substrate under the conditions typical of initial stage of epitaxial growth of doped ECD CdHgTe layers, and also in order to study substrate's structural perfection after short-term high-temperature treatment.

The comparison of initial and implanted morphology of crystal surfaces (Fig. 2) shows that after implantation the roughness had decreased from 6.4 to 2.9 nm. This can be a consequence of partial isotropic sputter-

ing of substrate's material, which is inherent to the ion implantation process.

The shapes of rocking curves taken in implanted and unimplanted regions of the crystal differ significantly before the annealing (Fig. 3a). One can observe a major widening of the main peak and formation of an additional shifted peak in the curve taken in the implanted region (Fig. 3a-2). The rocking curves given in Fig. 3a (1 and 2) indicate the formation of a layer with major disordering of the crystal structure, which introduces significant tensions on the crystal surface. The method based on the Fourier analysis of diffraction reflection curves was used for quantitative analysis [5]. Conducted calculations indicate that estimated width of the layer with major disordering which was formed on the CdTe surface (111) during the As ion implantation at room temperature, lies between 0.3÷0.35 μm, and the general region of structural defects extends to 0.6÷0.8 μm from the surface.

During the short-term high-temperature annealing the implanted impurity (Fig. 3b) not only diffuses into the middle part of the crystal, but also migrates into the region with the highest concentration of defects. Simultaneously, its profile shifts to the surface, that is, in the near-surface region (at the distance ~0.1 μm) where a major gettering of As takes place. The impurity profile, with the exception of near-surface region (~0.25 μm), has a classical Gaussian distribution form. By comparing half-widths of rocking curves from the implanted part of the sample before (Fig. 3a-2) and after (Fig. 3a-3)

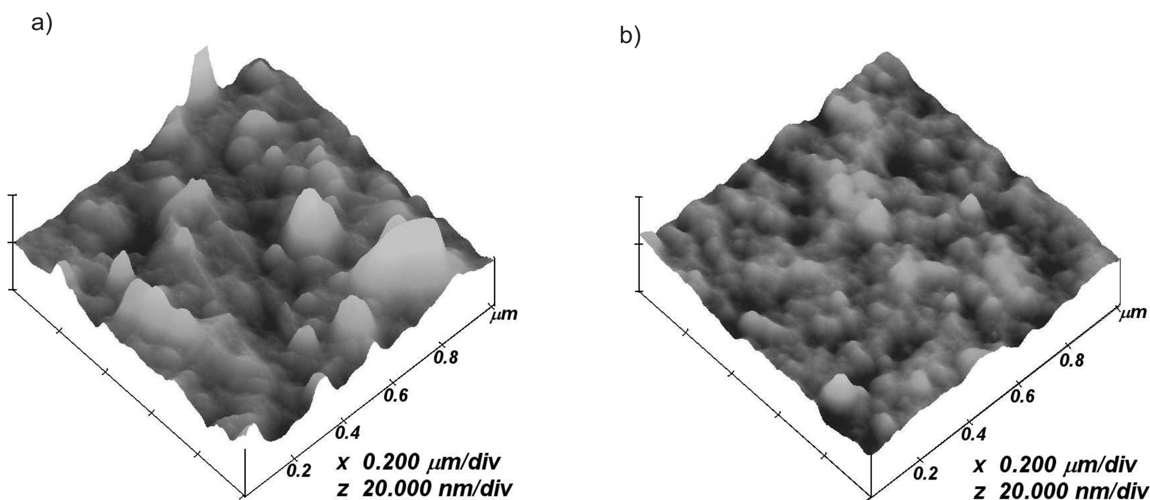

Fig. 2. The AFM topograms (1×1 μm^2) of the changes in morphology of CdTe (111) surface before (a) and after (b) implantation of the impurity: in the ranges of crystal surface after final chemical treatment (a) and subsequent implantation of As (b)

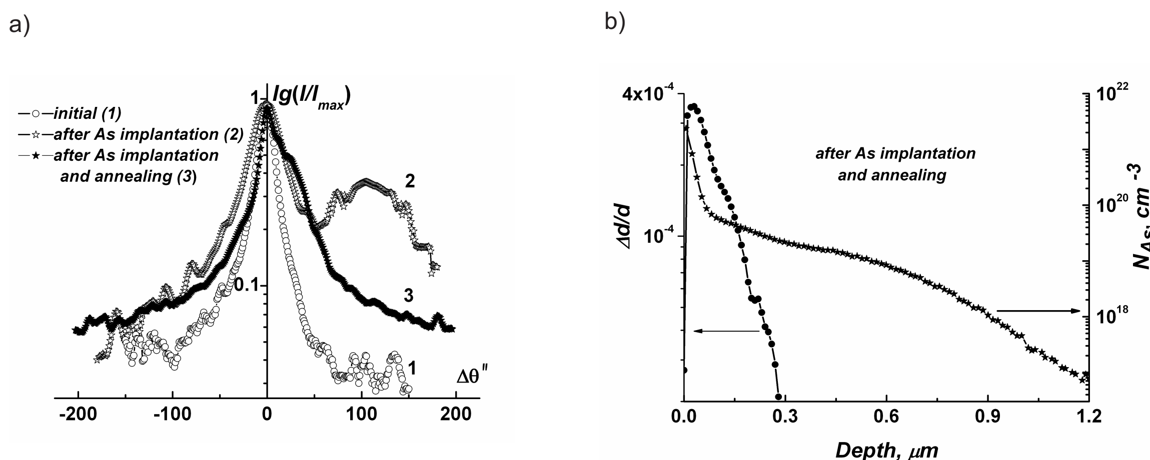

Fig. 3. Reconstruction of crystal structure of CdTe (111) surface. Rocking curves of diffraction reflection of CdTe single crystal: Cu$K\alpha$-radiation, symmetric scheme of diffraction, (111) incidence, (333) reflection – (a). Profiles of deformation and impurity distribution in the near surface region of CdTe (111) crystal after As implantation and annealing – (b)

annealing, one can notice that crystal structure of CdTe surface has been significantly improved i.e., there occurs a healing of radiation defects and many dislocations in near-surface regions of the crystal annihilated.

For determination of the depth distribution of strains in the near-surface layer we have used approaches based on the basic principles of the dynamic theory of X-ray scattering, namely, the numerical solutions of the Takagi differential equation system and comparison of the obtained results with the experimental data [6]. The calculated profile of deformation and corresponding SIMS profile of the impurity distribution in the near surface region of CdTe single crystal after As implantation and annealing are demonstrated in Fig. 3b. One can see that after annealing residual deformations exist in the near-surface regions, the extent of which correlates with the width of the impurity gettering region near the free surface of the implanted crystal.

For the next series of experiments we used the CdHgTe epitaxial layers doped with As during the ECD growth process, with the impurity in the CdTe (111) and CdTe (110) substrates being implanted with the same energy and dose.

3.2. ECD epitaxy of CdHgTe on the As implanted surface of crystalline CdTe substrate

Immediately after ion implantation and with no additional chemical treatment, CdTe substrates were mounted into quartz ampoules and loaded into furnaces in order to conduct ECD growth of epitaxial layers and their after-growth thermal treatment. The purpose of these experiments was the observation of influence of ion channeling processes in CdTe(110), which takes place at ion implantation into non-densely packed crystal lattice of sphalerite type [4], on the impurity distribution after ECD epitaxial growth of CdHgTe. The initial shape of impurity source changes in CdTe substrate (110) due to ion channeling effect. In comparison with the use of solid-state impurity source created on the CdTe substrate (111) after ECD epitaxy this leads to the changes in resulting profile of impurity distribution and correspondingly to the changes of concentration of electrically active acceptor impurity in the grown variable band-gap CdHgTe epilayer.

After ECD growth of CdHgTe on CdTe substrate (111) we have obtained a layer with the surface that has epitaxial growth terraces on it. Peculiar feature of the morphology of the sample studied by means of AFM lies in the fact that its surface structure is similar to that obtained by the authors of paper [7] on the surface of as-grown LPE CdHgTe epilayer on CdTe substrate (111). This means that such a surface structure (Fig. 4a) is inherent to the epitaxy of CdHgTe on CdTe substrates with (111) crystallographic orientation. The composition of the surface of CdHgTe solid solution grown by ECD epitaxy is equal to x_s = 0.19. The acceptor concentration $|N_A - N_D|$ = 1.7×10^{16}cm^{-3} (μ_H = 368 cm^2/(V·s)) in this sample correlates with the concentration of incorporated As that was determined by SIMS (Fig. 4b), thus the majority of As atoms is in the acceptor state. The given profile of impurity distribution (Fig. 4b) along the structure thickness shows that significant part of the impurity resides within the interface (initial surface of CdTe with the implant). Moreover, the greater part of impurity diffuses into the CdTe substrate (111), and the grown layer is uniformly doped.

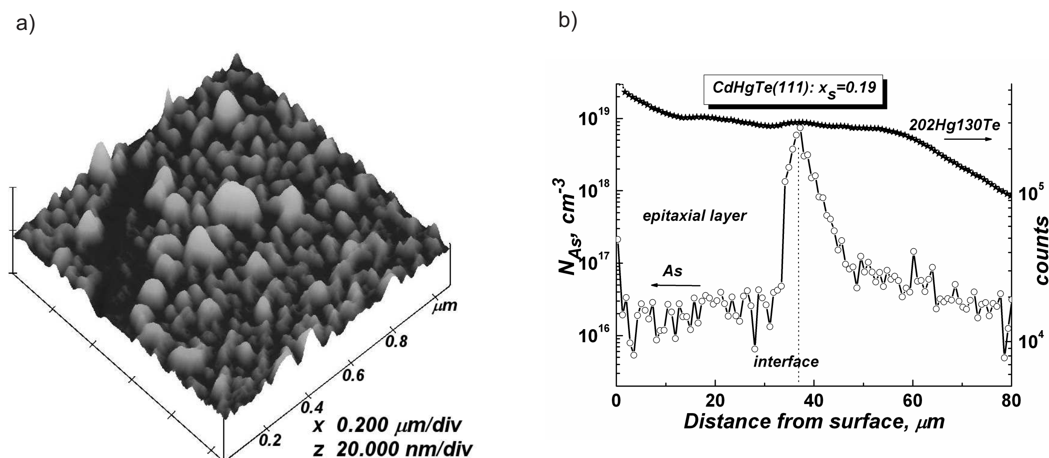

Fig. 4. AFM topogram (1×1 μm^2) of surface of CdHgTe graded-gap epitaxial structure grown on As-implanted substrate of CdTe (111) – (a) and the corresponding SIMS profiles of the impurity distribution and signal of the main component of CdHgTe solid solution on the thickness of the grown layer – (b)

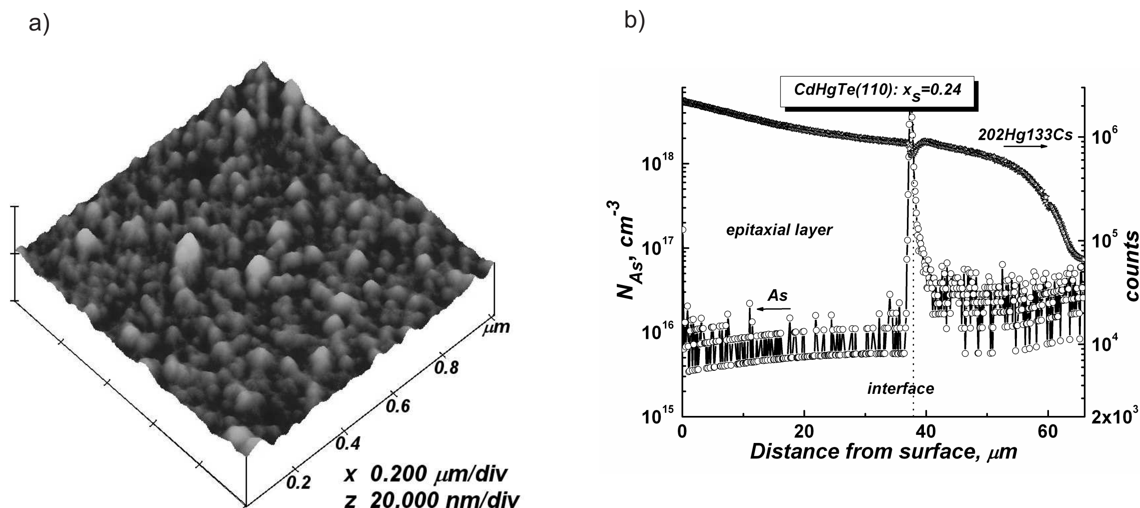

Fig. 5. AFM topogram (1×1 μm^2) of surface of CdHgTe graded-gap epitaxial structure grown on As-implanted substrate of CdTe (110) – (a) and the corresponding SIMS profiles of the impurity distribution and signal of the main component of CdHgTe solid solution on the thickness of the grown layer – (b)

As is seen from Fig. 5a, the epitaxial layer of CdHgTe grown on (110) CdTe substrate has better surface morphology, as opposed to the previous case (RMS roughness = 2.7 nm). The composition of CdHgTe solid solution on the surface of the sample was equal to $x_s = 0.24$, and the acceptor concentration in the epitaxial layer $|N_A - N_D| = 1.2\times10^{16}$cm^{-3} ($\mu_H = 518$ cm^2/(V·s)) also correlates with the concentration of incorporated As (Fig. 5b). The particular shape of impurity distribution profile along the thickness of the grown layer did not change significantly as compared to the distribution profile in the epitaxial layer grown on the implanted CdTe substrate (111). By comparing SIMS profiles of As distribution in samples grown on CdTe (110) and CdTe (111) substrates, that have equal quantities of the impurity implanted, it is obvious that obtained doping level is higher in ECD epilayer of CdHgTe with the (111) crystal orientation. Besides, the impurity source within the interface in the sample with crystal orientation (110), as opposed to the sample with orientation (111), is on the limit of exhaustion. Such a difference between SIMS profiles of the impurity distribution is probably caused by ion channeling effect occurring during the impurity implantation into the non-densely packed lattice of the (110) CdTe crystal.

The X-ray topogram analysis shows that the grown layers have a perfect crystal structure. This means that annihilation of radiation defects and recrystallization of near-surface disordered layers in the crystal sublattice of CdTe occur at the initial stages of the ECD epitaxy and do not deteriorate the crystal structure of the grown variable band-gap CdHgTe epitaxial layers.

4. Conclusions

The structural defects in disordered regions of radiation damages, which are created during the As implantation with an energy of 100 keV in the near-surface layers of CdTe single crystal substrates at irradiation doses of $D = 1\times10^{15}$ cm^{-2}, annihilate at the initial stages of epitaxy and virtually do not influence the structural perfection of the grown CdHgTe variable-gap epitaxial layers. Comparison of the results of AFM and X-ray diffraction structural investigations with the SIMS analysis that was carried out on similarly obtained As doped CdHgTe epitaxial layers (111) and (110), shows that the crystalline quality and topology of the surface in the samples with crystalline orientation (110) is higher. On the other hand, the level of As-doping along the thickness of the grown layer is lower, what is caused by the ion channelling during implantation into the non-densely packed crystalline lattice of CdTe crystal surface.

REFERENCES

[1] A. Rogalski, Defence Science Journal **51**, 1, 5 (2001).
[2] A. Vlasov, V. Pysarevsky, O. Storchun, A. Shevchenko, A. Bonchyk, H. Pokhmurska, A. Barcz, Z. Swiatek, Thin Solid Films **403-404**, 144 (2002).
[3] V. G. Savitsky, O. P. Storchun, Thin Solid Films **317**, 105 (1998).
[4] R. G. Wilson, J.Appl.Phys. **63**, 11, 5302 (1988).

[5] S. A. Stepanov, E. A. Kondrashkina, A. N. Chuzo, Poverkhnost'. Fizika, Khimiya, Mekhanika **9**, 112 (1988), (In Russian).
[6] P. H. Kyutt, Metallofizika i Novejshyie Tekhnologii **24**, 4, 497 (2002), (In Russian).
[7] J. D. Benson, J. B. Varesi, A. J. Stoltz, E. P. G. Smith, S. M. Johnson, M. Jaime-Vasquez, J. K. Markunas, L. A. Almeida, J. C. Molstad, J. Electron. Mater. **35**, 6, 1434 (2006).

Received: 10 April 2007.