



Diffusion in Si/Ge multilayers

Ph.D. dissertation

THESIS

Attila Csik

University of Debrecen
Debrecen, 2002

Introduction

Multilayers and superlattices, with thickness of few nanometers, are of considerable experimental and theoretical interest because of their specific properties (e.g. magnetic, electronic, mechanical and optical) and many promising areas of applications. These properties are usually related to the high interphase density and sometimes to the additional defects (grain boundaries, dislocations, mismatch stresses, etc.). However, the multilayers as artificial, compositionally modulated materials are not equilibrium structures. In particular, sufficient atomic mobility even at moderated temperatures, hence changes in the composition profile are expected to occur. Thus, investigation of the factors controlling structural changes of these multilayers is very important for the interpretation of their operation and prediction of their lifetime.

Since most structural changes are related to atomic diffusion, any real understanding of the structural transformation, homogenization, etc., must be based on the knowledge of the diffusion processes. Sophisticated preparation techniques nowadays make the fabrication of multilayers with almost atomically sharp interfaces possible. Thus, they can be used as ideal systems to check theoretical models (e.g. spinodal decomposition, diffusion along distances comparable to the atomic spacing, effects of as grown and diffusion induced stresses, interfaces migration, interfaces diffusion). For examples the lowest bulk diffusivities (down to 10^{-27} m²/s) can be measured by multilayer techniques.

Aims

In this work a detailed analysis was given regarding the strong concentration dependence of the diffusion coefficients in amorphous multilayers. It is based on experimental results obtained by small angle X-Ray diffraction (SAXRD), Transmission Electron Microscope (TEM), Rutherford backscattering (RBS) and Auger-depth profiling. The dissertation contains new results in the following areas:

- Experimental results confirm the theoretically predicted strong concentration dependence of the interdiffusion coefficient in amorphous Si/Ge system. The interdiffusion coefficient was determined from the change in the small angle X-ray diffraction satellites intensities.
- Direct experimental evidences on the diffusion asymmetry in Si/Ge multilayers were given by RBS and Auger depth profiling technique.
- Laser and heat induced optical changes were investigated in amorphous multilayers. Common features of stimulated structural transformations were discussed. Characterization of mechanism of the light- or heat-induced structural changes and interdiffusion as well as their interrelation with the optical parameters were also given.

Results

- Interdiffusion in amorphous Si/Ge multilayers, produced by DC magnetron sputtering with different modulation wavelength (2-9 nm) and nearly equal thickness of sublayers, was investigated. Experimental results, obtained from small angle X-ray diffraction, show a significant initial curvature on the $\ln I/I_0$ vs. t curve (I/I_0 is the normalized height of the first-order small angle X-ray diffraction peak, t is the time). The origin of this behavior previously was attributed to the effects of structural relaxation and stresses. From our experimental results, which was confirmed by theoretical calculations, can be clearly seen that the origin of this curvature is due to a concentration dependence of interdiffusion coefficient rather than to the structural relaxation.
- The theoretically predicted and experimentally indicated (by X-Ray diffraction and Rutherford backscattering measurements) thickening of the Ge layer was shown by Auger depth profiling technique. The results clearly show that the diffusion is very asymmetric: during annealing the silicon could enter into the germanium layer but the germanium could not diffuse into the silicon; at the same time, due to the silicon diffusion the germanium layer become thicker. It was also clear that during the heat treatment the sharpness of the interface remained the same. These results clearly indicated that the diffusion coefficient should strongly depend on the concentration and consequently measurements based on the SAXRD of multilayers could not be interpreted by neglecting non-linear effects. It was shown that it was possible to determine the concentration dependence of diffusion coefficient from plot of the $\ln I/I_0$ vs. t curves.
- The changes of optical parameters of amorphous Si/Ge multilayers during heat treatment and laser illumination was investigated. The results were compared to previous results on chalcogenide glasses (AsSe , $\text{Se/As}_2\text{Se}_3$). In amorphous Si and Ge single layers we could not detect noticeable changes under illumination, while the photo darkening was observed in single chalcogenide layer (As, Se). Blue shift of optical absorption edge was observed in all as-deposited multilayers, which can be connected with quantum-confinement effects. With decreasing thickness of the “valley” layers, and/or with the appearance and growth of intermixed layers due to interdiffusion, further shift and further bleaching of the multilayers was observed.
- It is shown that the blue-shift of the fundamental absorption edge in as-deposited compositionally modulated amorphous Si/Ge and $\text{As}_6\text{Se}_{94}/\text{Se}_{80}\text{Te}_{20}$ multilayers is further enhanced due to the thermal or laser-induced intermixing of adjacent layers. The laser-induced intermixing process, as supported by experiments and model calculations, can be attributed to both the local heating and photo-effects in $\text{As}_6\text{Se}_{94}/\text{Se}_{80}\text{Te}_{20}$ multilayers, while only the thermal effects were observed for Si/Ge multilayers. Structural transformations, based on this enhanced interdiffusion, provides good capability for spatially patterning optoelectronic devices and digital information recording.

Publication

- [1] **A.Csik**, D.L.Beke, G.A.Langer, Z.Erdelyi, L.Daroczi, K.Kapta, M.Kis-Varga „Non-linearity of diffusion in amorphous Si-Ge multilayers” *Vacuum* 61 (2001) 297
- [2] A.Simon, **A.Csik**, F.Pászti, Á.Z.Kiss, D.L.Beke, L.Daroczi, Z.Erdelyi, G.A.Langer „Study of interdiffusion in amorphous Si/Ge multilayers by Rutherford backscattering spectrometry” *Nucl. Inst. and Methods B* 161-163 (2000) 472
- [3] **A.Csik**, G.A.Langer, D.L.Beke, Z.Erdelyi, M.Menyhard, A.Sulyok „Interdiffusion in amorphous Si/Ge multilayers by Auger depth profiling” *J. of Appl.Phys.* 89/1 (2001) 804
- [4] D.L.Beke, A.Dudas, **A.Csik**, G.Langer, M.Kis-Varga, L.Daroczi, Z.Erdelyi „On the thermal stability of multilayers” *Functional Materials* 6 (1999) 539
- [5] D.L.Beke, G. A.Langer, **A. Csik**, Z.Erdélyi, M.Kis-Varga, I.A.Szabó, Z.Papp „Diffusion and thermal stability in multilayers” *Defect and Diffusion Forum* 194-199 (2001) 1403-1416
- [6] **A. Csik**, M.Malyovanik, J.Dorogovics, A.Kikineshi, D.L.Beke, I.A.Szabo, G.Langer „Photo-stimulated structural transformations and optical recording in amorphous semiconductor multilayers” *J. of Optoelectronics and Advanced Materials* 3 (2001) 33
- [7] M.Malyovanik, S.Ivan, **A.Csik**, G.A.Langer, D.L.Beke, S.Kökényesi „Laser induced optical changes in amorphous multilayers” Submitted to *J. Appl. Phys.*

- [8] **A.Csik**, A.Simon, J.Nyeki, G.A.Langer, D.L.Beke, E.Gabor, L.Daroczi „Effect of hydrostatic pressure on the crystallization and spinodal decomposition in amorphous Si/Si_{20%}Sb/Si system” *A Conference on Modern Microscopical Methods* Innsbruck, 9-14 september (2001), Poster presentation
- [9] M.Malyovanik, J.Dorogovich, M.Shipljak, A.Kikineshi, **A.Csik**, M.Kis-Varga „Vacuum thermal deposition and optical properties of chalcogenide glass based nanostructures” *Functional Materials* 6, No. 3 (1999) 482
- [10] J.Lindenmajer, N.Hegman, S.Meszaros, K.Vad, G.Langer and **A.Csik** „RF susceptibility of magnetron sputtered YBa₂Cu₃O_{7-x} films” *Vacuum* 50, No. 3-4, (1998) 413