Nanoscale Fast Ge Diffusion in Laser Irradiated SiGe Thin Films

V.S. Teodorescu[*], C. Ghica[*], A.V. Maraloiu[*], A.M. Lepadatu[*], I. Stavarache[*], M.L. Ciurea[*]
[**]N.D. Scarisoreanu[**], A. Andrei[**] , M. Dinescu[**]

[*] National Institute of Material Physics, 105 bis Atomistilor Street, 077125 Bucharest-Măgurele, Romania, teoval@infim.ro, cghica@infim.ro, maraloiu@infim.ro, lepadatu@infim.ro, stavarache@infim.ro, ciurea@infim.ro
[**] National Institute of Plasma Lasers and Radiation, 409 Atomistilor Street, 077125 Bucharest-Măgurele, Romania, snae@nipne.ro, dinescum@nipne.ro, andreic@yahoo.com

ABSTRACT

We report the presence of a fast Ge diffusion effect produced during laser crystallization of $Si_{0.45}Ge_{0.55}$ films deposited by magnetron sputtering on Si(100) substrates. The laser irradiation was performed using the 266 nm wavelength radiation of the Nd-YAG laser. After the irradiation with 10 laser pulses at a fluence of 30 mJ/cm^2 the top part of the film shows two zones. Zone I, with a thickness of about 20 nm is crystallized and rich in Ge. The next zone in depth, i.e. Zone II, of about 30 nm thicknesses, has a mixed quasi-amorphous structure and is deficient in Ge, as the EDX scan-line analysis reveals. This cannot be explained considering the usual value of the Ge diffusivity in SiGe and the short time of the laser heating. The redistribution of Ge by fast diffusion suggests a real diffusion coefficient of the order of magnitude of 10^{-4} cm^2/s, which is an usual value for liquids. However, in this zone, the SiGe structure was not melted by the laser pulse irradiation.

Keywords: laser irradiation, SiGe thin films, Ge diffusion, transmission electron microscopy, AFM

INTRODUCTION

Laser processing of the thin films is a well known method for developing new technologies. SiGe is an interesting material from both technological and fundamental point of view, with applications in band-gap tailoring, solar cells and non volatile memory devices. The Ge nanocrystallite formation in SiGe, Ge:Si or Ge:SiO_2 mixed systems or other dielectric matrix is intensively studied in the last decade for quantum well devices. In some cases, pulse laser processing has been applied [1-10]. In all these systems, the diffusion of Ge is an important factor related with the formation and stability of the nanostructure. The Ge diffusion in the SiGe system was studied in details [11-13]. However, some aspects related to the changes in nanostructures made by Ge diffusion are not well known or not yet understood.

One of the advantages of the pulse laser annealing is the limited time of the heating and the limited diffusion length associated with. It is well known that the species diffusion length is $(\mathbf{D\tau})^{1/2}$, were **D** is the diffusion coefficient of the atomic species in the matrix and $\boldsymbol{\tau}$ is the time duration of the laser pulse. Under normal conditions, if **D** is of the order of magnitude of 10^{-14} cm^2/s [12] and $\boldsymbol{\tau}$ about 10 ns, the diffusion length becomes less than one picometer, so practically there is no diffusion. However, the diffusion takes place at the nanometer scale in condition of a high number of laser pulses, leading to formation of a large variety of surface nanostructures [14-16], mainly due to Ge diffusion to the top layer of the laser target. Laser irradiation of SiGe films at small laser fluence value leads to the formation of a network of nano-areas reached in Ge on the film surface [14]. The goal of our experiment is related to the study of the laser crystallization of amorphous SiGe films. We report on a new interesting Ge diffusion effect obtained in pulsed laser irradiation experiments made on $Si_{0.45}Ge_{0.55}$ films deposited on Si(100) wafer substrates.

EXPERIMENTAL

The SiGe thin films with a thickness of 170 nm were prepared by magnetron sputtering deposition using a co-sputtering from two targets of Si and Ge, respectively. The deposition was performed on Si[100] wafers and carried out in Ar atmosphere at a pressure of 4 mTorr [6]. The chosen Si:Ge composition is 45:55. The as deposited SiGe films structure is amorphous and is presented in Fig 1. The laser irradiations were performed in air perpendicular to the film surface using the 266 nm radiation of the Nd-YAG laser. The laser beam on the sample was round with a 7 mm diameter and homogenious in intensity with a local variation less than 10%. The laser fluence used for the experiments was varied between 20 and 50 mJ/cm^2. The structure of the SiGe films before and after laser irradiation experiments was studied by transmission electron

microscopy (TEM) and atomic force microscopy (AFM), using a Park XE100 apparatus. The TEM specimen preparation was performed by cross section technique using the tripod method. The final ion milling of the specimens was made in a Gatan Precision Ion Polishing System Model 691. The TEM specimens were observed using a Jeol ARM 200F electron microscope. The XTEM specimens were oriented in the <110> zone axis for precise thickness measurements, as it can be seen in SAED inserted in Fig.1.

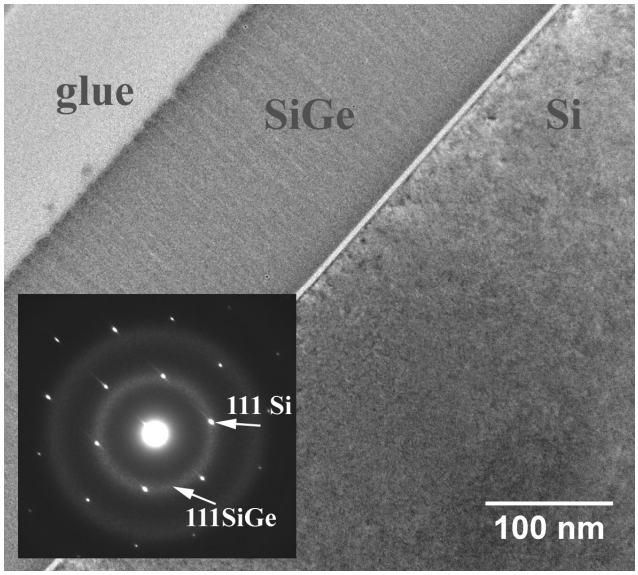

Figure 1. The XTEM image and the inserted SAED pattern of the as deposited (before laser irradiation) SiGe amorphous film on the Si substrate in <110> orientation .

RESULTS AND DISCUSSIONS

The laser irradiation area of the SiGe film was chose to be clean, free of any visible defects. The surface control was made by optical microscopy and AFM. After laser irradiation, the morphology of the film surface has not visible changes. As we can see in the AFM image (Figure 2a), the roughness of the surface is similar to the surface relief of the film before irradiation shown in the XTEM image in Figure 1. The surface morphology features have been preserved after laser irradiation as revealed by the low magnification XTEM image sown in Figure 3a. This is an indication that the surface was not melt during laser pulse irradiation. The fluence threshold value for melting was determined to be higher than 40 mJ/cm^2, the surface film relief has visible changes above this value (see Figure 2b).

After laser irradiation with 10 pulses at the fluence of 30 mJ/cm^2, the XTEM images show structural modifications which appear at the top part of the SiGe film, revealed in Figures 3 and 4. The top part of the film shows two zones. Zone I has a thickness of about 20 nm and is crystallized. The SiGe nanocrystallite size in this area is between 15 and 25 nm. The following zone II has a mixed crystalline and quasi-amorphous structure and is extended about 30 nm in the film depth. The rest of the film remains amorphous (zone III in Figure 3 ande 4). The absorption coefficient for the amorphous SiGe at 266 nm can be considered to be similar to the one of amorphous Si or Ge, which are of the order of magnitude of 10^6 cm^{-1} [18]. In this case we expect to have an absorption length of about 10 nm and consequently the laser radiation is absorbed in the thickness of the zone I.

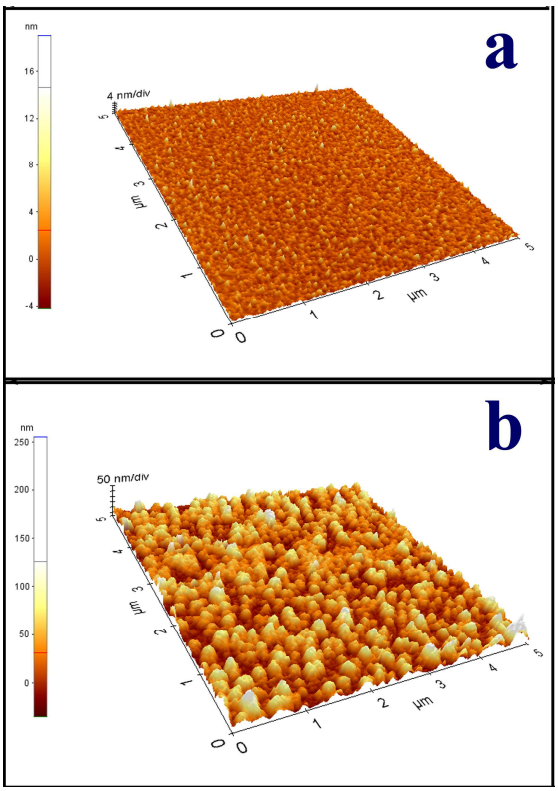

Figure 2. AFM image of the irradiated area of the SiGe film: a- after 10 laser pulses at a 30 mJ/cm^2 fluence ; b- after 20 laser pulses at 42 mJ/cm^2 fluence

The interesting feature of the experiment is reveled in Figure 4, which shows the XTEM and the dark field STEM images of the same area of the film section, as well the corresponding EDX scan-line analyze of the film after laser irradiation. The EDX analyze shows a strong segregation of the Ge in the top layer (zone I) followed by a Ge deficient layer in the embedded zone II.

This feature is not possible to happen if we consider valid the usual value of the diffusion coefficient of Ge in SiGe which is about 10^{-14} cm^2/s (at about 1000K) [3] and the total time duration of the hot top layer of the film, which is not more than 300 ns. However, the redistribution of Ge by fast diffusion really happened, which leads to a diffusion coefficient of about 10^{-4} cm^2/s. This fast diffusion can happen only in liquid [3]. However the estimation of the top film temperature at the laser fluence of 30 mJ/cm^2 is far

from the melting point of the SiGe structure, if we consider the usual absorption coefficient of 10^6 cm^{-1}. The real absorption coefficient should be higher and the zone I is probably heated near the melting point, which for the SiGe 45:55 is expected to be around 1450K [11]. In any case , the area of the zone II, which is the Ge depleted zone, is not heated near melting point. This result shows that in the presence of laser pulse field, a fast diffusion effect takes place in solid state phase.

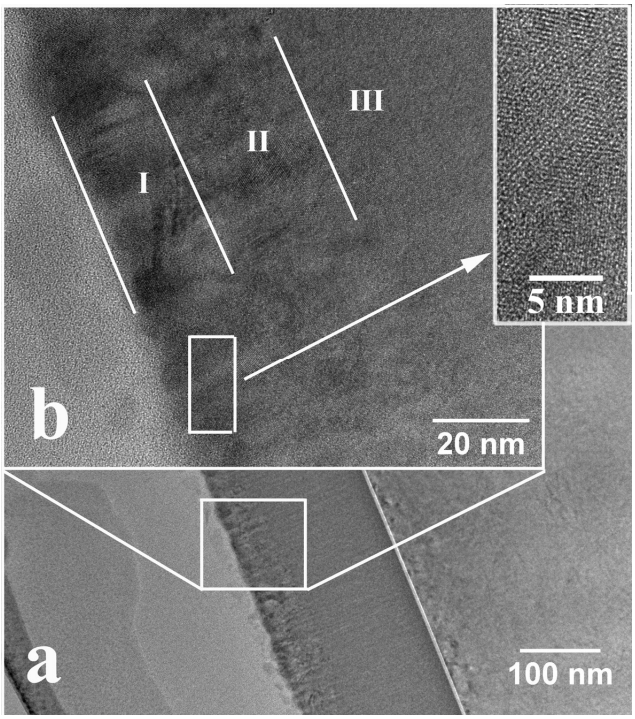

Figure 3. The XTEM image (a) and the high magnification details (b) of the SiGe film structure after the laser irradiation with 10 pulses at the fluence of 30 mJ/cm^2

If we look at the distributions of oxygen, germanium and silicon in Figure 4c, we observe relative maxima of the oxygen located at the boundary between the zone I and zone II together with a minimum of the Ge content. The Ge segregation phenomenon was reported [19-20] in the case of classical oxidation of SiGe structure. So, because in our case, the Irradiation takes place in air, the oxygen has also a fast diffusion in the film structure during laser irradiation.

A structural feature characteristic for the films obtained by sputtering is the columnar morphology. This columnar morphology is present also in the case of amorphous films, like in our case. The boundaries between columns are a less dense local structure, allowing higher species diffusivity in the direction normal to the film. Even so, the Ge diffusion remains in solid state phase, which is much limited than in liquid phase and is not enough fast to explain the observed Ge segregation in our case.

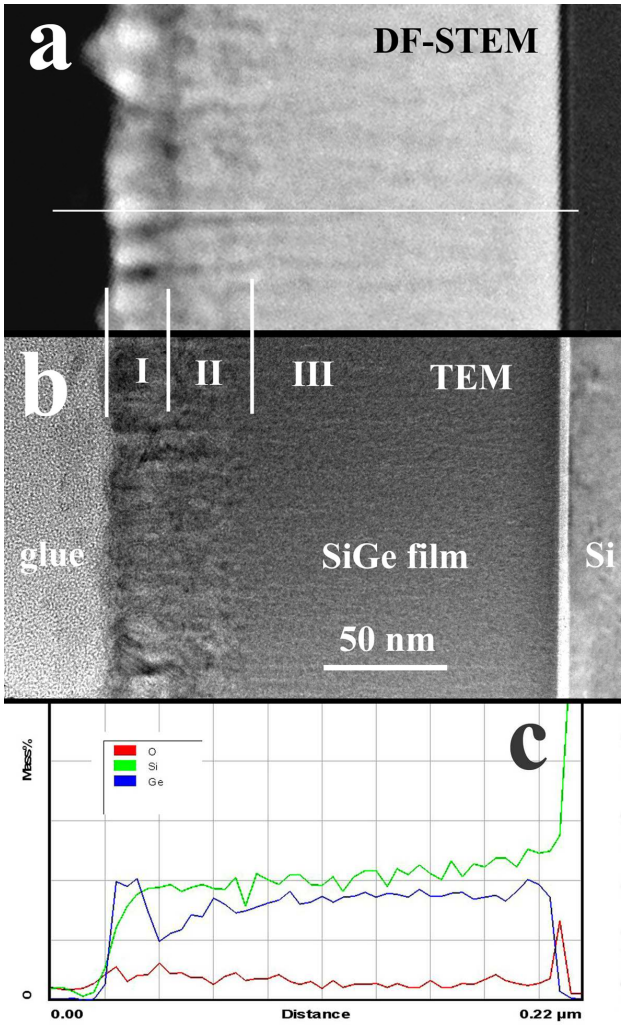

Figure 4. The DFSTEM (a) and the TEM (b) images of the same area of the film section and the corresponding EDX line analyze (c) for the SiGe thin film irradiated with 10 laser pulses (266 nm) at the 30 mJ/cm^2 fluence. The film structure is changed in the thickness of about 50 nm with two distinguished zones: a crystallized zone I of about 20 nm thicknesses at the top surface of the film and a zone II extended about 30 nm in the film depth, which can be considered a thermally affected region. The crystallized zone at the top film surface is rich in Ge extracted by diffusion from the zone II.

CONCLUSIONS

The laser crystallization experiments performed on amorphous SiGe thin films obtained by magnetron sputtering show the unconventional Ge diffusion in the surface layer of the laser irradiated film. The Ge content of the top crystallized layer of the SiGe film is higher compared with the average SiGe film content. The thickness value of this top crystallized layer is of the order

of magnitude of the absorption length of the laser radiation in the SiGe structure (zone I). The layer located under the top crystallized one, is less crystallized or quasi-amorphous and is depleted in Ge. This layer (zone II) is less heated than the top crystallized one. The Ge diffusion in this area takes place in solid state phase, which is normally negligible during the laser pulse heating time. However, the Ge diffusion length in this area is between 10 and 20 nm corresponding to a diffusivity of about 10^{-4} cm^2/s. This is the characteristic diffusivity value for a melted SiGe matrix.

We conclude that the diffusion is enhanced in solid state matrix in the presence of the laser pulse field, which also have a larger penetration depth in the film compared with the laser absorption length.

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