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Influence of Hydrogen on the Structural Stability of Annealed Ultrathin Si/Ge Amorphous Layers

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Abstract. The influence of hydrogen on the structural stability of multilayers made of ultrathin (3 nm) Si and Ge amorphous layers submitted to annealing to activate Si and Ge intermixing has been studied by TEM and AFM. By energy dispersive microanalysis the interdiffusion of Si and Ge has been observed. The Si/Ge multilayers, however, underwent remarkable structural degradation because of the formation of hydrogen bubbles which give rise to surface bumps and eventually craters when the bubbles blow up because of too high internal pressure in samples with high H content and annealed at high temperatures. The hydrogen forming the bubbles comes from the rupture of the Si-H and Ge-H bonds activated by the thermal energy of the annealing and by the energy released by the recombination of thermally generated electron hole pairs.

Introduction

Hydrogen, with its single electron and its small covalent radius, can be used to compensate individual dangling bonds in Si, Ge and SiGe alloys. Hydrogenation can thus improve the electro-optical properties of those materials, in particular for their application as solar cells, by reducing the deep electronic levels in the band gap [1-4]. In this regard, hydrogenated amorphous SiGe alloys (a-SiGe:H) are being investigated for use as low band gap material in multijunction solar cells [5-7]. The band gap of a-SiGe:H can in fact be modulated between 1.1 and 1.75 eV by changing the Ge composition or H content which allows a better exploitation of the solar spectrum [5, 7]. A solar cell made of a-Si:H/a-SiGe:H junction absorbs both the high energy portion of the spectrum with a-Si:H (band gap energy 1.75 eV) and the low energy portion with a-SiGe:H (band gap energy in the range 1.10 to 1.75 eV).

One way of preparing the amorphous hydrogenated SiGe alloy is to deposit very thin alternating layers of Si and Ge and then form the alloy by intermixing the Si and Ge elements via diffusion [8, 9]. This requires heat treatments. The question is thus raised what is the stability of

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hydrogen against heat treatments. The behavior and instability of H in a-Si:H, a-Ge:H and a-SiGe:H has been studied mostly with reference to its effects on the electro-optical properties [5, 6, 10-16]. Much work exists for samples submitted to light soaking for which degradation of the electro-optical performances was ascribed to the de-passivation of the dangling bonds because of H desorption [5, 12-14]. The influence of the H behavior on the structural properties has little been investigated, just for light soaked samples [12-14]. It is shown here that also thermal treatments can cause structural changes. The investigated materials are hydrogenated a-Si/a-Ge multilayers prepared by sputtering and subsequently submitted to annealing.

Experimental

Ultrathin (thickness 3 nm) alternating amorphous layers of Si and Ge were deposited on water cooled (100) Si substrates by radio frequency sputtering in an argon atmosphere (purity 99.999 %) of 2.0 Pa. The crystalline Si and Ge targets were powered at 1.5 kV. The samples consisted of multilayer stacks made of 50 pairs of Si/Ge layers for a total thickness of 300 nm. Hydrogenation was carried out by letting hydrogen to flow into the deposition chamber with different flow rates, namely at 0.8, 1.5, 3 and 6 ml/min. The samples were annealed in high purity (99.999%) argon atmosphere at 350, 400 or 430 °C for 1 h, 9.5 or 16 h. A more severe annealing in two steps at 250 °C for 0.5 h and then at 450 °C for 5 h was also applied. Not-hydrogenated samples sputtered and annealed under the same conditions of the hydrogenated ones were also investigated.

The structural investigations were performed with atomic force microscopy (AFM) in tapping mode and transmission electron microscopy (TEM) with a JEOL 2200 FS instrument. The TEM was equipped with a high angle annular dark field (HAADF) detector with convergence angle of 11 mrad and collection angle of 46 mrad for a camera length of 10 cm. In a HAADF experiment the intensity of the scattered beams is proportional to Z^n with Z the atomic number and n very close to 2 [17]. Energy dispersive X-ray microanalysis (EDX) in the TEM was also employed. For both HAADF and EDX measurements an electron beam spot size between 0.5 and 1 nm was used. The cross-sectional specimens for TEM were prepared by sandwiching a slab of the sample between silicon pieces and subsequent mechanical thinning down to ˜30 μm. Final thinning to electron transparency was accomplished by argon ion milling.

Results and discussion

The structure of the amorphous Si/Ge multilayers is shown in the HAADF image of Fig. 1 which is representative of both not-hydrogenated and hydrogenated samples. Figures 2 and 3 are the EDX results for two samples submitted to heat treatment at 350 °C for 1 h and 9.5 h, respectively. After annealing at 350 °C for 1 h the EDX signals of Ge and Si are quite distinguishable though much more for Ge. The peaks of Ge emerge quite well from the background at well defined positions corresponding to the nominal Ge layers. For annealing for the longer time of 9.5 h the peaks of both elements are much more diffused out, especially those of Si, suggesting a greater interdiffusion of the elements.

The not-hydrogenated samples did not show any degradation of the surface morphology after annealing even after the most severe one, with an average rms roughness, as measured by AFM, on the order of 0.19 nm. On the contrary, the hydrogenated samples showed a significant surface degradation after annealing. Figures 4 a)-c) give the AFM results for 3 samples annealed at 350 °C, 16 h (H_2 flow 0.8 ml/min), 430 °C, 16 h (H_2 flow 1.5 ml/min) and at 250 °C, 0.5 h and then at 450 °C, 5 h (H_2 flow 6 ml/min), respectively. The surface rms roughness is 5.2, 14 and 133 nm, respectively. Samples annealed at intermediate conditions and hydrogen flow rates have intermediate stage of degradation. Surface degradation increases with increasing hydrogen content and time and/or temperature of annealing.

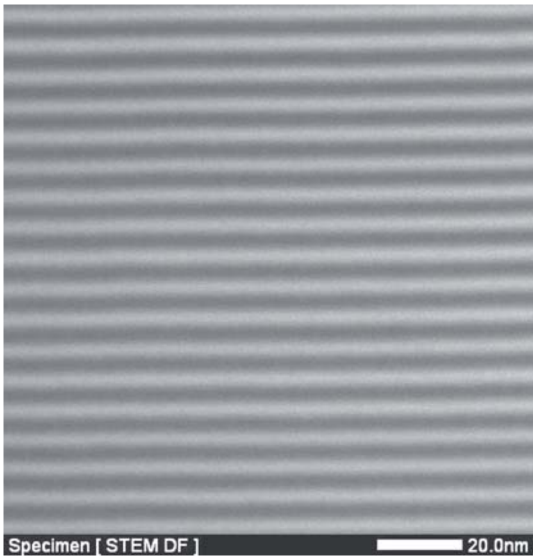

Fig. 1 – Typical HAADF image of the investigated amorphous Si/Ge multilayers. Central part of the multilayer. The substrate (outside the field of view) is on the bottom side of the picture. The Ge layers are the bright ones.

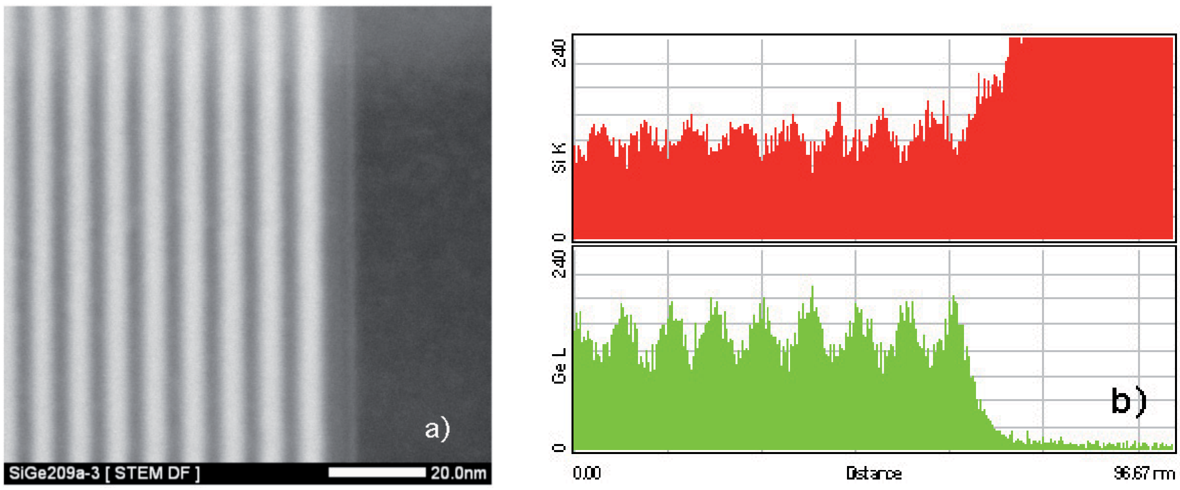

Fig. 2 – Si/Ge multilayer annealed at 350 °C for 1 h. a) HAADF image, b) EDX line scan profiles for Si (top) and Ge (bottom) across the zone in a). The Si substrate is visible on the right part of a).

The EDX results confirm that elements interdiffusion has occurred upon annealing. Si seems to have diffused more into the Ge layers than Ge into the Si ones, which is in agreement with previous works that used small angle X-Ray diffraction to evaluate the element intermixing [18-19]. In those works such asymmetry was ascribed to the strong concentration dependence of the interdiffusion coefficients.

The AFM results, however, show that degradation of the structure of the Si/Ge multilayers also occurs in the hydrogenated samples. It consists of surface bumps and craters. The craters are present in the annealed samples hydrogenated with the highest H flow rates and/or submitted to the most severe annealing treatments. By looking at Fig. 4 c) the conclusion can be drawn that the

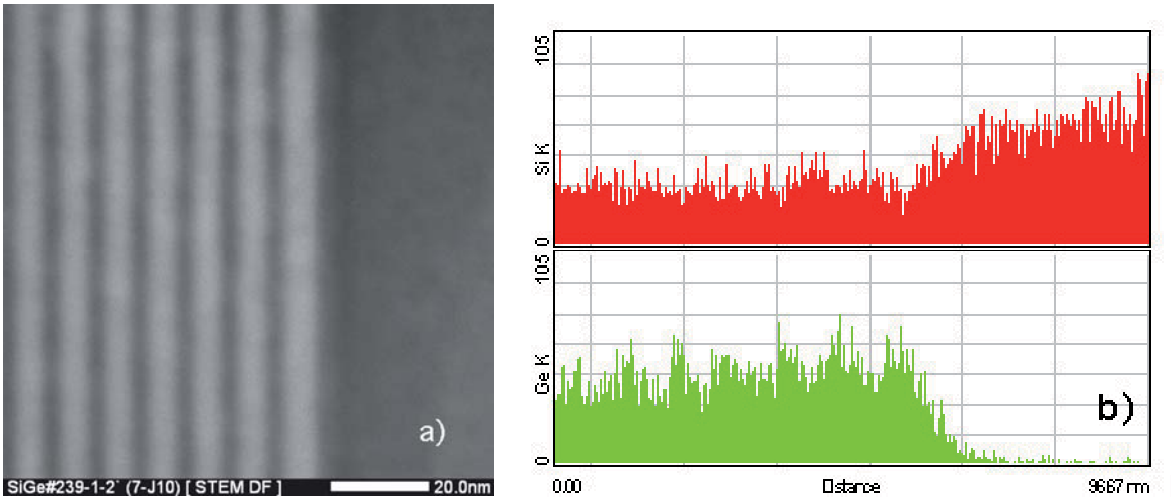

Fig. 3 – Si/Ge multilayer annealed at 350 °C for 9.5 h. a) HAADF image, b) EDX line scan profiles for Si (top) and Ge (bottom) across the zone in a). The Si substrate is visible on the right part of a).

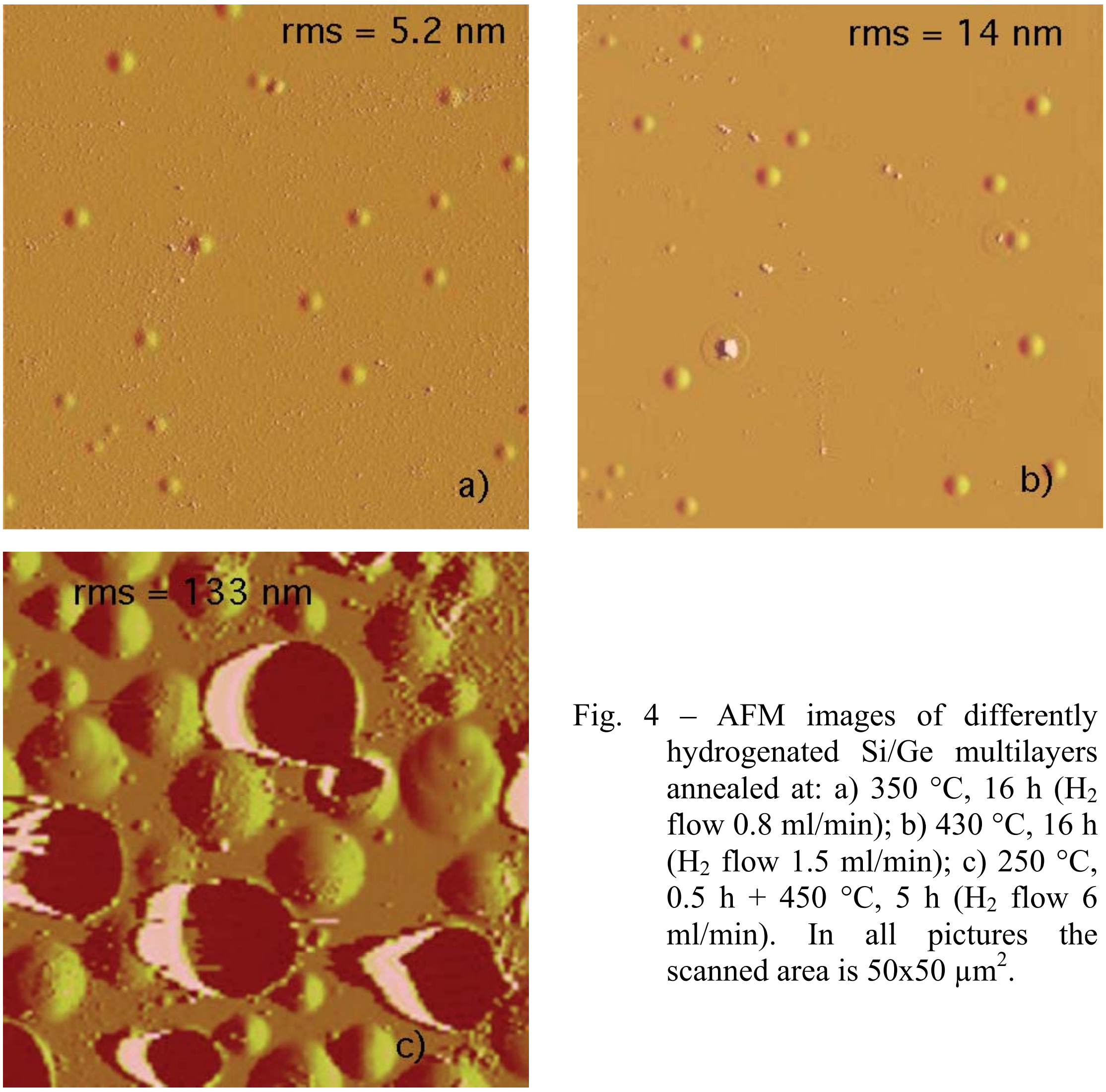

Fig. 4 – AFM images of differently hydrogenated Si/Ge multilayers annealed at: a) 350 °C, 16 h (H_2 flow 0.8 ml/min); b) 430 °C, 16 h (H_2 flow 1.5 ml/min); c) 250 °C, 0.5 h + 450 °C, 5 h (H_2 flow 6 ml/min). In all pictures the scanned area is 50x50 μm^2.

craters are bumps which have blown up. Since the craters are empty it can be hypothesized that the bumps are bubbles filled with some gas, namely hydrogen. The formation of the hydrogen bubbles requires the availability of free, not bonded hydrogen.

Apart from the free hydrogen atoms not bonded to any Si or Ge host atom during the multilayer deposition, the main supply of free hydrogen is expected to come from the rupture of the Si-H and Ge-H bonds because of the energy supplied by the thermal treatments. This leads to the formation of H_2 molecules as proposed by Beyer by studying the effusion of hydrogen from a-Si [3, 10] according to the scheme of Fig. 5. Formation of hydrogen bubbles should initiate by

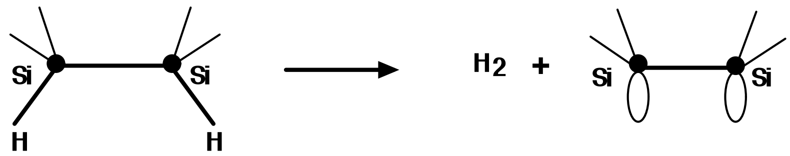

Fig. 5 - Sketch displaying the rupture of two Si-H bonds leading to the formation of a H_2 molecule and the creation of two unsaturated dangling bonds. The same holds for the Ge-H bond.

the gathering together of the H_2 molecules at nanocavities, very likely present in amorphous materials as suggested by Beyer [3, 10]. Such nanocavities are also expected to be the first places where H breaks its bonds to Si or Ge [4, 10]. Additional energy for the rupture of the H bonds can be provided by the thermally generated carriers [11]. The very likely inhomogeneous distribution of H present in our samples can cause local band gap variations, with the zones of less hydrogen content having the smaller band gap [11, 14]. This inhomogeneous band gap structure can make the thermally generated carriers to drift to the regions of small band gap and recombine there with consequent release of energy [11]. The growth in size of the bubbles can be favored by the presence of interconnections among the nanocavities along which the H_2 molecules can quickly diffuse thanks to the thermal energy supplied by the annealing. The bubbles are obviously the biggest in the samples containing more hydrogen. They also become very large for the most severe heat treatments because a high temperature makes the H_2 gas bubbles to become bigger by the gas law.

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