Selective ultrashort laser annealing of amorphous Ge/Si multilayer stacks

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Abstract. We report on single-short laser crystallization of Ge/Si multilayer stacks consisting of alternating amorphous nanosized films of silicon and germanium using near- and mid-infrared femtosecond and picosecond laser pulses. The phase composition of the irradiated stacks was investigated by the Raman scattering technique. Several non-ablative regimes of crystallization were found, from partial crystallization of germanium without intermixing the Ge/Si layers to complete intermixing of the layers with formation of Ge_xSi_{1-x} solid alloys. The roles of one- and two-photon absorption, thermal and non-thermal (ultrafast) melting processes, and laser-induced stresses in selective pico- and femtosecond laser annealing are analysed based on theoretical estimations and comparison with experimental data. It is concluded that, due to a mismatch of the thermal expansion coefficients between the adjacent stack layers, efficient explosive solid-phase crystallization of the Ge layers is possible at relatively low temperatures, well below the melting point. The possibility of ultrafast non-thermal phase transition in germanium in the studied regimes is also discussed.

1 Introduction

Low-temperature crystallization of thin amorphous semiconductor films is in high demand for fabrication of “flexible electronics” devices. Recently, germanium thin films with a record-high hole mobility were obtained on flexible plastic using post-growth annealing at relatively low temperature of 500 ºC [1]. However, for using inexpensive plastic flexible substrates, it is necessary to reduce their heating to temperatures below 120 ºC. Pulsed laser annealing appears to be the only suitable technique for crystallization of amorphous semiconductor films without overheating substrates [2,3].

A number of attempts were made to selectively crystallize germanium in amorphous Ge/Si multilayer (ML) systems. However, usually laser annealing leads to intermixing of Si and Ge layers and to formation of their alloy. Recently, we achieved successful selective crystallization of germanium layers in an amorphous Ge/Si ML stack using picosecond 1030-nm laser annealing [4]. In the present study, we have extended the irradiation conditions to longer wavelength (1500 nm) and shorter pulse duration (70 fs) and compared ps and fs annealing regimes with the aim to find optimal conditions for selective crystallization of Ge layers in Ge/Si ML stacks without crystallization of silicon and intermixing Ge and Si layers.

2 Experimental

Multilayer a-Si:H/a-Ge:H stacks consisted of 4 Si (40-nm thick) and 3 Ge (15-nm thick) alternating amorphous layers were produced by plasma enhanced chemical vapor deposition on a Si(100) substrate. Monosilane (SiH_4) and monogermane (GeH_4) gases were used as precursors for the Si and Ge layers.

The produced Si/Ge stack were annealed by a ps laser (HiLASE PERLA-B, λ=1030 nm, pulse duration 1.4 ps) and by an fs laser (Astrella, Coherent) in combination with an optical parametric amplifier (TOPAS, Light Conversion) delivering a beam at λ=1500 nm with a pulse duration of 70 fs. The beams were focused at normal incidence on the sample surface onto circular spots of diameters of 2.1 mm for 1030 nm and 0.53 mm for 1500 nm. The laser fluence F_0 was varied in the range 20-200 mJ/cm^2. The phase composition of as-deposited and annealed ML stacks was studied by Raman spectroscopy using a T64000 spectrometer with micro-Raman setup. The excitation 514.5-nm laser beam was focused to a 10-µm-diam spot at the center of the annealed spots and thus the Raman spectra were collected from sites annealed uniformly at the peak laser fluence F_0.

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3 Results and discussion

Figure 1 shows Raman spectra obtained after irradiation of the Si/Ge MLs at low laser fluences for fs and ps pulses. The Raman spectrum of the as-deposited ML stack is also shown. The latter contains broad bands at ~480 cm^{-1} and ~275 cm^{-1} indicating that all the layers are completely amorphous. The spectrum of the as-deposited MLs has no features of the vibration frequencies of Ge–Si bonds (in range from ~390 cm^{-1} to ~440 cm^{-1}) pointing that the concentration of such bonds is too low to be detected.

The laser treatment of the Si/Ge stack at F_0 below 50 mJ/cm^2 for fs pulses and 40 mJ/cm^2 for ps pulses does not lead to changes in the Raman spectra, indicating no noticeable structural transformations in the ML samples. Ps irradiation at F_0 = 46 mJ/cm^2 results in appearance of a narrower feature at a frequency of ~ 296 cm^{-1} against the background of the amorphous component (see Fig. 1). The analysis shows that the observed Raman shift of ~5.5 cm^{-1} corresponds to the average size of Ge nanocrystals (NCs) of about 3 nm [5]. In the case of fs pulses at 64 mJ/cm^2, the NC-Ge peak is higher and narrower, and its position corresponds to the average NC size of ~4.5 nm. No peaks corresponding the Si crystalline phase have been observed.

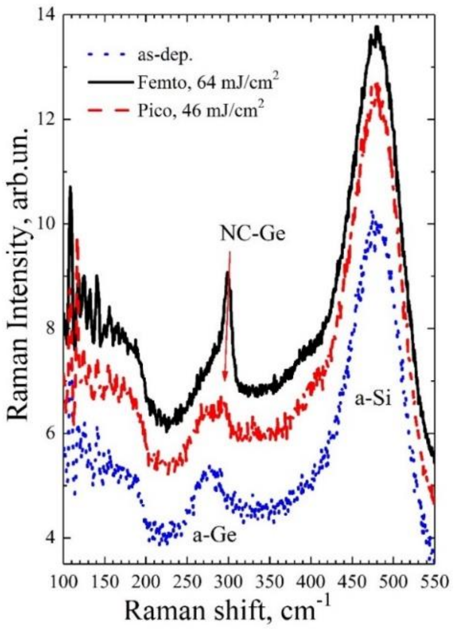

Fig. 1. Raman spectra of as-deposited and low-fluence laser annealed Si/Ge ML stack. The arrow shows a small peak of Ge nanocrystals produced by ps laser pulses.

At $F_0 \geq$ 70 mJ/cm^2, the Ge layers are already almost completely crystallized but the Raman spectra show slight intermixing with the silicon layers. Starting from 100 mJ/cm^2, silicon crystallizations is observed while, at $F_0 \geq$ 150 mJ/cm^2, a strong peak of Ge-Si bonds appears in the Raman spectra indicating formation of a Ge-Si alloy.

We have analysed the major processes induced by ultrashort laser pulses in amorphous Ge and Si layers under the conditions of our experiments and considered their consequences for Ge/Si multilayer stacks. This includes laser ionization kinetics in Si and Ge under excitation by ultrashort near-infrared laser pulses, heating of a-Ge and a-Si layers, their melting and melt fraction, and laser-induced thermal stresses. The analysis is based on the ionization rate equations, energy balance, and the theory of thermoelasticity.

It has been found that the laser energy directly absorbed by Si layers can provide only a slight heating much below the melting point. At the same time, Ge layers experience strong ionization close to or higher than the critical plasma density. Interestingly, for ps laser pulses, Ge ionization is provided by one-photon absorption while, in fs ionization regime at the wavelength of 1500 nm, two-photon absorption plays a significant role in generation of a so-called solid plasma.

According to the energy balance analysis for ps laser pulses at F_0 below ~70 J/cm^2, partial melting of germanium occurs that should lead to formation of NC-Ge phase without affecting the Si layers. At slightly higher fluences, increasing the fraction of molten germanium may lead to the formation Ge-Si bonds at the interfaces between the layers. Irradiation with laser fluences ≥ 100 J/cm^2 provides complete melting of the Ge layers and their heating well above the melting point. As a result of the heat transfer from Ge to Si layers, the latter may receive enough heat for partial or even complete melting that depends on laser fluence and the adjacent molten layer should experience interdiffusion.

At fs irradiation regimes, the theory shows that a-Ge layers start to melt only at fluences of ~100 J/cm^2. However, estimations of thermal stresses yield the high values up to 0.97 GPa at 100 mJ/cm^2 and we note that such a level of stresses can cause solid-phase explosive crystallization of the Ge layers at low laser fluences [6]. Additionally, the evaluated levels of the density of electron-phonon pairs can induce destabilization of the amorphous lattice leading to ultrafast nonthermal phase transition that however calls for further studies.

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