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Full Length Article

Silicon and silicon-germanium nanoparticles obtained by Pulsed Laser Deposition

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ABSTRACT

Semiconductor nanoparticles are of great interest in the area of microelectronics and can also be used in many optoelectrical devices as for example optical converters for photovoltaic applications.

Silicon (Si) and silicon-germanium (SiGe) quantum dots can be used as high-energy photon converters, known as "red-shift" photoluminescence (PL) in solar cells in order to improve their efficiency. We report on the possibility to produce SiGe nanoparticles by Pulsed Laser Deposition (PLD) on silicon dioxide substrates. We keep the focus on the control of morphological properties of nanoparticles considering various deposition parameters like temperature, fluence and the amount of deposited material. $Si_{0.5}Ge_{0.5}$ controlled ratio is obtained by optimizing the amount of matter ablated successively from Si and Ge pure targets. Rutherford Backscattering Spectroscopy (RBS) is used to confirm the stoichiometry of the deposited structures. Morphological characterization is performed by Atomic Force Microscopy (AFM), determining average diameter, height and density of the nanoparticles. In order to confirm the crystalline character of the deposited particles, Raman analyses have been performed, helping in determining the optimal deposition temperature. PLD allows to condense a very small and controlled amount of material during the deposition process, permitting this way the growth of nanostructures in a 10 nm range. With these dimensions, SiGe quantum dots are subject to have a photoluminescent (PL) behaviour. However, no photoluminescence is observed on the deposited nanoparticles.

1. Introduction

In Si-based solar cell technology, there exists two main optical mechanisms leading to an efficiency loss of the photoconversion behaviour. The first one is the inability to absorb photons having an energy lower than the band gap. The second point is related to the thermalisation effect as well as high-energy UV photons, which do not contribute to the photocurrent. Therefore, specific layers on the top of solar cells containing structures able to convert high-energy photons (making them contribute to the photocurrent) could improve their efficiency as it has been already demonstrated [1–5].

To achieve such a photoconversion process, semiconductor nanoparticles, nanocrystals or quantum dots, directly linked to a photoluminescence mechanism are already used [3,6–8]. In our case, we focus on the possibility of converting UV photons into visible or infrared light. This conversion is known as "red-shift" or "down-shift" photoluminescence [3,6,7].

The photoluminescence behaviour directly depends on the nanoparticle structures [3,7–11], meaning that controlling size and density of the particles allow to tune their optical properties. These are directly related to the technique and experimental parameters used to create them [9,11,12]. The PLD technique permits high flexibility by offering control over a large panel of parameters such as fluence, substrate nature and temperature, pulse repetition rate and target-substrate distance.

In this study, we use PLD to produce Si and SiGe nanoparticles by control of the Si and Ge ratio and the structure of the deposited layers (particle size and density).

2. Experimental details

2.1. Pulsed laser deposition setup

Laser deposition is performed using a Lambda-Physik COMPEX 201 excimer laser with a KrF gas mixture (248 nm, 25 ns pulse duration). The beam is focused through two cylindrical lenses onto high purity targets placed in a high vacuum chamber, typically in the 10^{-8} mbar range (thanks to a turbomolecular pump). A precise measurement of

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the focused beam hitting the target surface (1.09 mm^2, determined by measuring the laser impact dimensions on a silicon wafer) allows the determination of the fluence range, varying from 2 to 15 J/cm^2. The laser repetition rate is settable from 1 to 10 Hz. Si and Ge pure targets (electronic-grade purity) are mounted on a holder attached to a slow rotation speed motor (1 rpm). The incoming laser beam is focused on the target with a 45° incidence angle. However, the emitted species are ejected perpendicularly to the surface and reach the substrate, placed parallel to the target surface at a fixed distance of 5 cm. The substrate temperature can be set to values up to 650 °C during the deposition process.

To control the stoichiometry of the deposited layers, Si and Ge massive targets are mounted side by side and are ablated alternatively. The number of successive laser shots on each target during a full rotation of the holder is directly correlated to the beforehand measured ablation rate of each element to obtain as precise as possible, a $Si_{0.5}Ge_{0.5}$ controlled ratio in the layers.

To allow coalescence during the deposition process, epitaxial growth on the substrate surface has to be avoided. Therefore, 1 × 1 cm^2 Si ⟨1 0 0⟩ substrates were covered by a thermally grown dry SiO_2 (50 min at 1100 °C under pure oxygen atmosphere). The measured thickness of the oxide (67 nm) was determined by spectroscopic ellipsometry. However, pure Si substrates offering a very low surface roughness (1 nm) were also used with the only goal of determining the deposition rates of each element during preliminary experiments. Before installing the substrate in the PLD chamber, each sample is cleaned with ethanol in an ultrasonic bath.

2.2. Characterization techniques

The surface morphology was characterized by AFM with a 256 × 256 pixels resolution over a 1 × 1 μm^2 surface. For each sample, AFM and image software analysis permits us to determine the morphology of the nanoparticles regarding their diameter and height. Several measurements are performed on the same sample in order to extract an average value for each dimension. In addition, the density and the surface coverage were also determined from the images analysis.

Raman spectroscopy is a widely used characterization method for exploring the binding between atoms in a crystalline structure. In the case of Si and SiGe nanoparticles, the crystallization level of the deposited layer can be quantified [19,20]. Some studies also report the possibility of direct particle size determination using peak shift measurements of the different peaks in the Raman spectra [11,21] (when compared to the reference positions of bulk crystalline Si and SiGe). JOBIN YVON LabRam Aramis was used with a 532 nm laser excitation focused on the sample surface with a 100 magnification objective. The laser spot size has a diameter of 0.4 µm with a maximum energy of 40 mW. For all our measurements, the energy was limited to 4 mW and the acquisition varies from 1 to 60 s depending on the sample response. This setup allows an energy resolution less than 0.5 cm^{-1}.

In order to obtain the composition (silicon and germanium relative percentage) of the deposited alloys, we use Rutherford Backscattering Spectroscopy (RBS). This non-destructive analysis technique is based on a sample interaction with light ions (α particles at 1 MeV energy in our case). Corresponding composition is deduced by direct comparison between the spectra with simulation.

3. Results and discussion

3.1. Ablation rate determination

As shown in the literature, one of the main PLD drawbacks is the possible presence at the substrate surface of undesirable macroparticles ejected from the target during the deposition process. In order to decrease their amount, a specific study on the deposition rate of each material has been realized for various experimental conditions. Furthermore, it is well known that Si and Ge do not have the same ablation behaviour. Indeed, the relative deposition rate of each material has to be precisely determined [12–14]. Later, this parameter will ensure a stoichiometric control of the deposited alloy.

We have determined deposition rates at three different fluences (2.5, 5 and 10 J/cm^2). For each element and at each fluence, deposition is performed on Si substrates for a given time. The layer thicknesses are measured by profilometry (Dektak 150). Deposition rates are calculated by dividing the measured thicknesses by the number of laser pulses used to produce them. Our results clearly show that the deposition rates for Si and Ge approach a linear increase as a function of the fluence. We observe that the Ge deposition rate nearly reaches twice the one of Si.

As it well known, PLD of semiconductors leads to the formation of a high number of undesirable macroparticles (larger than 1 µm) ejected from the target during the deposition process. In order to drastically reduce this unwanted emission of material, we explored PLD at two different laser pulse frequencies (1 and 10 Hz). We observed a different behaviour between the two frequencies. At 1 Hz, the deposited surface shows a very low amount of droplets compared to 10 Hz (at least 20 times less). Indeed, during a process performed at 10 Hz, two successive laser shots induce an impact superposition of almost 90% on the irradiated target. In comparison, a shooting frequency of 1 Hz will drive to only 10% overlap (Fig. 1). This variation induces a very different behaviour in the laser-material interaction process. In fact, repeated laser shots at the same place leads to a strong local degradation correlated with an important emission of macroparticles. Therefore, working at a 1 Hz ablation rate permits to obtained high quality depositions.

Furthermore, an effect of laser fluence was also observed. Therefore, we performed our depositions at the best fluence conditions (2.5 J/cm^2) on which the macroparticles density is even more reduced. Therefore, in the following study, we consider a deposition rate of 0.014 Å per pulse for Si and 0.022 Å per pulse for Ge by working with a 2.5 J/cm^2 fluence at 1 Hz.

3.2. Nanoparticles growth

Nanoparticles formation obeys to a coalescence phenomenon. Coalescence is a complex mechanism depending on various parameters such as material density, surface roughness, size of existing particles and temperature [15–18]. We focus our study on the effect of temperature. For depositions performed at room temperature up to 400 °C, the Si and the SiGe alloy remains an amorphous compound with a low surface roughness kept in the nm range (from 1 to 3 nm). Room temperature deposited samples were used as reference to evaluate the Equivalent Deposited Material Amount of Si and SiGe (EDMA). We observe that the coalescence starts when the substrate surface temperature is set to values over 400 °C. Previous studies have shown that working at higher temperature leads to a particle size increase correlated to a density decrease [16]. A similar behaviour is observed when nanoparticles are grown by other techniques such as chemical vapour

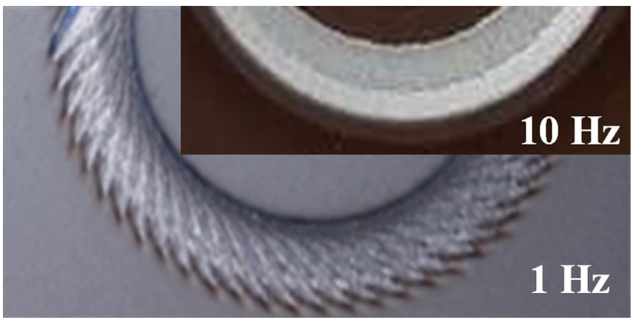

Fig. 1. Visual comparison of the silicon target surface for 1 and Hz laser shot repetition rates.