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Shadowed off-axis production of Ge nanoparticles in Ar gas atmosphere by pulsed laser deposition: Morphological, structural and charge trapping properties

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ABSTRACT

In this work, a novel customized shadowed off-axis deposition set-up is used to perform an original study of Ge nanoparticles (NPs) formation in an inert Ar gas atmosphere by pulsed laser deposition at room temperature varying systematically the background Ar gas pressure (P_{base}(Ar)), target–substrate distance (d) and laser repetition rate (f). The influence of these parameters on the final NPs size distributions is investigated and a fairly uniform droplets-free and non-agglomerated NPs distribution with average height $\langle h \rangle = 2.8 \pm 0.6$ nm is obtained for optimized experimental conditions (P_{base}(Ar) = 1 mbar; d = 3 cm; f = 10 Hz) with a fine control in the NPs density (from 3.2×10^9 cm^{-2} to 1.1×10^{11} cm^{-2}). The crystalline quality of as-deposited NPs investigations demonstrate a strong dependence with the Ar gas pressure and a crystalline to amorphous phase volume fraction $\chi_c > 50\%$ is found for P_{base}(Ar) = 2 mbar. The NPs functionality for charge trapping applications has been successfully demonstrated by capacitance–voltage (C–V) electrical measurements.

1. Introduction

Semiconductor quantum dots/nanoparticles (NPs) present unique size-dependent physical properties for many applications in optoelectronics, non-volatile memories and solar cells [1–5]. In comparison with Si NPs that have been widely investigated during the last two decades [3,5–9], the interest in Ge NPs has been increasing during the last years due to Ge advantages in respect to Si such as a larger Bohr exciton radius, lower band-gap (strong confinement), larger carrier mobility and higher band-gap sensibility to NPs size variations [10]. Although a lot of work has been dedicated to the chemical synthesis of Ge NPs with promising results [11,12], several constraints still remain especially for applications in the microelectronic technology because of the presence of organic ligands (as surfactants) and it usually requires a multi-step production process [11]. The production of Ge NPs embedded in dielectric oxide matrices has been carried out by many deposition techniques such as magnetron sputtering [13], ion implantation [14], thermal/electron induced evaporation [9,15] and plasma-enhanced chemical vapour deposition [16]. The NPs self-assembling in the dielectric host matrix is usually obtained through a post-deposition annealing step of a Ge-rich oxide matrix [17] or a Ge layer [18]. Although this process can lead to the formation of a relatively well layered structure of Ge NPs between dielectric oxide layers, Ge out-diffusion from the film or Ge diffusion between alternated layers cannot be ruled out even at relatively low temperatures (700 °C) in either Al_2O_3 or SiO_2 matrices [19–21]. In comparison with high temperature (800–1000 °C) and long (>30 min) conventional furnace annealing treatments, rapid thermal annealing (RTA) has been successfully demonstrated as an effective short-time thermal treatment for these purposes [22,23].

In contrast to other techniques, pulsed laser deposition (PLD) is a versatile technique for the growth of high quality thin films

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and nanostructured materials that offers the possibility of a contaminants-free synthesis process of nanoparticles (NPs) in a one-step process at room temperature (RT) when an inert/reactive gas atmosphere is introduced in the deposition chamber. The PLD synthesis of NPs in different inert and reactive gas atmospheres has been widely demonstrated mostly for Si [7], while the production of Ge NPs in background inert gas atmospheres is less explored [24]. Experimental and theoretical results have demonstrated that the Si NPs distributions can be changed by controlling the experimental parameters such as background gas pressure [25], kind of background gas [26] or laser energy fluence [8]. However, there is some controversy in the results presented throughout the literature in terms of NPs size distribution that may be due to re-sputtering processes on the NPs film deposited on the substrate induced by direct deposition of droplets simultaneously deposited together with high energetic particles [27,28], hindering the actual morphology and distribution of NPs produced in the gas atmosphere. For example, Yoshida et al. [25] found that the average size of Si NPs increases monotonically with the background gas pressure, whereas Lowndes et al. [29] found a maximum average size for a critical pressure, that is attributed mainly to a different deposition/collection geometry. On the other hand, it is also well known that NPs agglomerates formation produced in a gas phase strongly depends on the experimental conditions used in the production process [30]. In this regard, for some practical applications like memory devices where obtaining well separated NPs on the substrate is mandatory, it would be desirable to optimize the PLD production process.

In this work, we have performed a systematic study of PLD Ge NPs production in an inert Ar gas atmosphere using a unique shadowed off-axis deposition geometry [31], that allows us to explore the Ge NPs formation process in the gas phase and optimize the PLD parameters (background Ar gas pressure P_{base}(Ar), target–substrate distance d and laser repetition rate f) in order to obtain functional droplets-free non-agglomerated NPs films while avoiding the influence of high energetic particles. The influence of the number of laser pulses for a given experimental conditions on the NPs density obtained on the substrate surface was studied. The NPs structural properties were evaluated on as-deposited at different P_{base}(Ar) values and post-processed by RTA samples. The charge trapping capabilities of the Ge NPs is discussed based on capacitance–voltage (C–V) electrical measurements performed on metal-oxide-semiconductor (MOS) structures where a well defined Ge NPs layer was embedded between thin amorphous Al_2O_3 layers.

2. Experimental

2.1. Samples fabrication

The PLD set-up used in this work is equipped with a KrF excimer laser (wavelength of 248 nm and 20 ns pulse duration) and a multi-target carrousel assembly which allows the deposition of different materials by moving different targets into and out of the laser beam focal point with no need to break the vacuum conditions. High purity (99.999%) Al_2O_3 and Ge targets were used. During deposition, the targets were rotated to maintain uniform material evaporation as much as possible. P-doped and low-resistivity Si (1 0 0) substrates (1–6 $\Omega\,cm^{-1}$) used in all the experiments were first dipped for 10 s in a HF:H_2O (10:1) solution for native oxide removal, rinsed in abundant deionized water and blown using dry N_2. Briefly, our experimental set-up consists of a mobile assembly as shown schematically in Fig. 1, which allows *on-axis* and *shadowed off-axis* (mask height = 0.6 cm) configurations for the deposition of Al_2O_3 and Ge NPs, respectively. More details about the technique can be found in Ref. [31]. The Al_2O_3 layers were deposited in high vacuum conditions ($P_{base} = 2 \times 10^{-7}$ mbar) with $d = 4$ cm and $f = 10$ Hz using the *on-axis* configuration. The laser energy fluence was kept constant in all the experiments to a value of 1.2 J/cm^2. For the Ge NPs production, an inert Ar gas atmosphere was introduced inside the growth chamber and the Ge target was ablated using the *shadowed off-axis* configuration. In order to study the influence of the PLD experimental parameters on the Ge NPs distributions, a set of samples was prepared varying the background Ar gas pressure, target–substrate distance and laser repetition rate.

2.2. AFM and SEM characterization

The morphological characterization was performed by AFM and scanning electron microscopy (SEM) on uncapped samples of Ge NPs deposited on Si (1 0 0) substrates where a 10-nm-thick amorphous Al_2O_3 thin film was previously deposited. This Al_2O_3 layer presents a very low root mean square (RMS) surface roughness value RMS $\sim$ 0.15 nm as measured by atomic force microscopy (AFM) and therefore, it was used as a good reference for the measurement of individual Ge NPs. The AFM measurements were performed in tapping mode using an AFM Nanoscope III set-up in ambient conditions and WSxM software was used for AFM data analysis [32]. SEM measurements were performed with a FEI Quanta400FEG ESEM system equipped with a EDAX Genesis X4M EDS system.

2.3. Micro-Raman spectroscopy

Micro-Raman spectroscopy is a non-destructive, fast and sensitive technique for crystalline and/or amorphous phase identification in nanometer-sized thin films of particles. The structural characterization was performed on tri-layer [Ge NPs/Al_2O_3 (10 nm)] $\times$ 3 structures deposited on 10-nm-thick Al_2O_3-coated Si (1 0 0) substrate. A Jobin-Yvon T64000 system with an optical microanalysis system and a CCD detector at room temperature using the 488 nm Ar^+ laser excitation line was used. The scattering spectra of the samples were recorded in backscattering geometry. The laser beam was focused on the sample surface with a beam spot size of 1 μm and a power of 0.5 mW to avoid the heating of the sample. Silicon TO mode at 521 cm^{-1} was used as calibration frequency reference.

2.4. Capacitance–voltage (C–V) measurements

High frequency (1 MHz) C–V measurements were performed on MOS capacitor structures with Ge NPs embedded in a tri-layer structure [Al_2O_3 oxide gate layer (20 nm)/Ge NPs/Al_2O_3 tunnel layer] at RT and 150 K with a Sula Technologies Spectrometer. If not stated the contrary, the tunnel layer thickness (t_{tunnel}) was kept constant to t_{tunnel} = 10 nm. A gold layer was deposited on the back-side surface of the p-type Si substrate by thermal evaporation to make an ohmic contact. Gold contacts on the front-side of the samples were prepared by Au thermal evaporation through a mask on top of the sample with circular openings (0.8 mm^2). Possible dynamic recharging effects during measurement were avoided using a ramp rate of 0.03 V/s. The samples were kept in a cryostat during measurements to minimize noise from external electromagnetic fields and photon-induced carrier excitation.

3. Results

In Fig. 2, SEM and high resolution AFM images of Ge particles distributions obtained varying the experimental parameters (number of laser pulses on Ge target n_p = 300 pulses) are shown. The average NPs height and their dispersion values were obtained