Effect of Nucleation Parameters of Ge Quantum Dots Grown over Silicon Oxide by LPCVD

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ABSTRACT

Germanium quantum dots (Ge-QD) were grown by Low Pressure Chemical Vapor Deposition (LPCVD) on Si nucleus previously grown on 3 nm thick SiO_2 ultra thin film. Samples were analyzed by atomic force microscopy (AFM) and high resolution transmission electron microscopy (HRTEM). We report the analysis of the influence of the nucleation parameters on size and spatial distribution of Ge-QD. AFM images show a Ge-QD density of around $3.6x10^{10}$ cm^{-2}, with an 11 nm mean size and 2.9 nm height. Finally, HRTEM investigation shows that the Ge-QD have a crystalline structure, i.e., they are nanocrystals.

Index Terms: Nanocrystals, nanostructures, quantum dots, germanium, LPCVD.

1. INTRODUCTION

In the last years, silicon, germanium or silicon–germanium quantum dots embedded in an insulator have been studied extensively for their mesoscopic behavior. They have potential applications not only for silicon-based optoelectronic devices, but also for room temperature operation of single electron memories [1]. Specifically, Ge nanocrystals embedded in a dielectric matrix (such as SiO_2) are now being extensively studied as the charge storage elements in flash memory devices [2], [3], [4]. It is known that due to quantum confinement effects these nanocrystals exhibit nonlinear optical properties that usually do not appear in the bulk materials.

Ge-QD can be obtained by various techniques, such as pyrolysis [5], co-sputtering [6], pulsed-laser ablation [7], ion implantation [8] and Low Pressure Chemical Vapor Deposition (LPCVD) [9]. All these techniques, besides the last one, require a high temperature annealing to produce the nanostructures. The synthesis of Ge-ns reported herein is based on a conventional CVD method [10] using a low base pressure (LPCVD). In the case of Si-QD, chemical vapor deposition (CVD) addresses these issues quite well [10], [11]. CVD is a robust, efficient, and industry-compatible method to deposit semiconductor films and nanocrystals. The successful CVD of Si-QD on oxide substrate is well known in the literature. However, CVD of Ge onto SiO_2 surfaces involves first creating Si nuclei for the subsequent growth of the Ge-QD [12]. The primary aim of this work is to understand the influence of nucleation parameters, namely, total pressure, temperature and precursor gas flow rate on the density and size of the obtained Ge-QD. Moreover, we also studied further the formation of Ge-QD on the obtained Si nuclei by alternately controlling the selective growth conditions in LPCVD using SiH_4 and GeH_4, both diluted in H_2. It is important to observe that in our study we demonstrate that crystalline quantum dots can be obtained by a technique that does not require high temperature annealing.

2. EXPERIMENT

The substrates used in this study are *p*-type Si (100) wafers covered by a 3 nm thick thermally grown SiO_2 layer. Si nuclei and Ge-QD were grown in a vertical LPCVD reactor (PMC 200), using SiH_4 and GeH_4 as precursors and H_2 as carrier gas. The hydroxylation of the thermal SiO_2 was performed using a 0.1% HF solution.

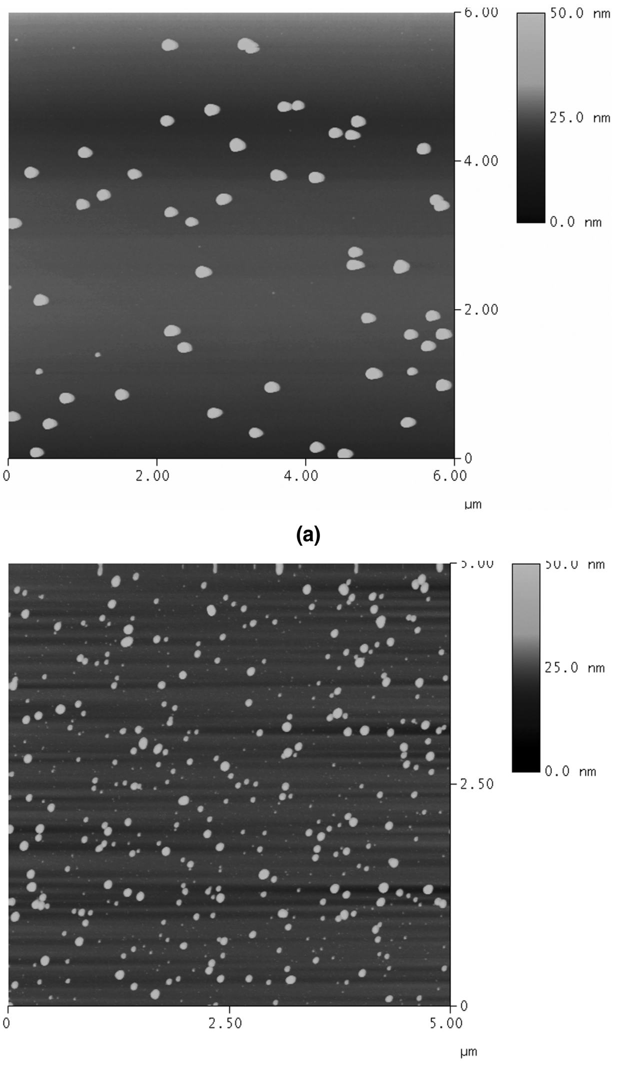
Ge-QD was grown in two-step process [13]. First, the SiO_2 surface was functionalized by deposition of Si nuclei using SiH_4 as gaseous precursor at temperatures of 550° C and 600° C; pressures of 2 and 5 Torr; nucleation time of 10, 20 and 30 sec.; and SiH_4 gas flow of 10, 20 and 40 sccm. Second, Ge-QD was grown selectively on the Si nuclei using GeH_4 gas. Before this step, the CVD chamber is purged to eliminate the residual SiH_4 gas, and the sample maintained under pure H_2 atmosphere, without oxidizing Si nuclei. The conditions for the selective Ge deposition on Si nuclei were kept as 550° C, 2 Torr, 30 sec. and 5 sccm GeH_4 gas flow.

The morphological characteristics, such as sizes and density of the Ge-QD were characterized by atomic force microscopy (AFM) using a DI Nanoscope IIIa microscope, as well as the high-resolution transmission electron microscopy (HRTEM), JEM-3010 ARP microscope, were used to verify the Ge-QD structure.

3. RESULTS AND DISCUSSION

Figure 1 (a) and (b) show AFM images of the surfaces of the Ge-QD deposited at nucleation temperatures of 550° C and 600° C, respectively. The other nucleation parameters were kept constant, namely, 5 Torr/40 sccm SiH_4/20 sec. We observed that on the sample prepared at 600° C, the Ge-QD density ($6.4x10^9$ cm^{-2}) is increased by about 21X, and their mean size (26 nm) is decreased by approximately 4X, compared to the sample deposited at 550° C. This increase in Ge-QD density can be attributed to the increase in the nucleation rate as a consequence of the larger surface energy. A possible explanation for size decrease could be the Ge-QD density increase, since in both cases GeH_4 flow is equal.

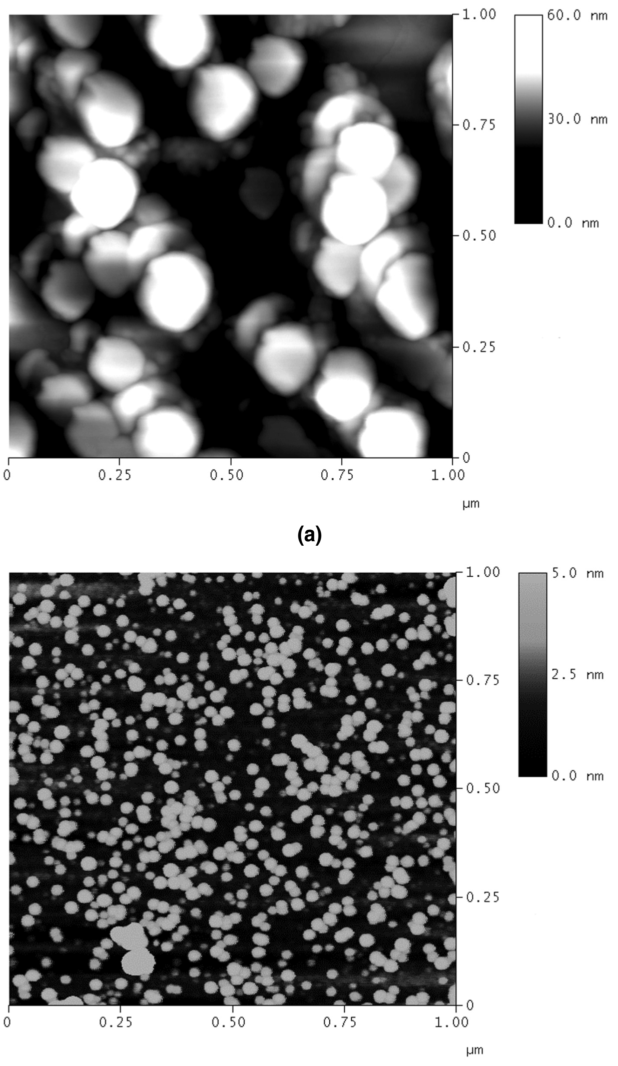
Figure 2 shows AFM images of Ge-QD samples deposited with two different growth pressures. These images show that increasing the total pressure from 2 Torr to 5 Torr, with the other parameters kept con-



(a)

(b)

Figure 1. AFM images of Ge-QD deposited under the sample conditions with the following nucleation temperatures: (a) 550° C, Ge-QD density = $3x10^8$ Ge-QD/cm^2, and (b) 600° C, Ge-QD density = $6.4x10^9$ Ge-QD/cm^2. The mean sizes are equal to 96 nm and 26 nm, respectively.



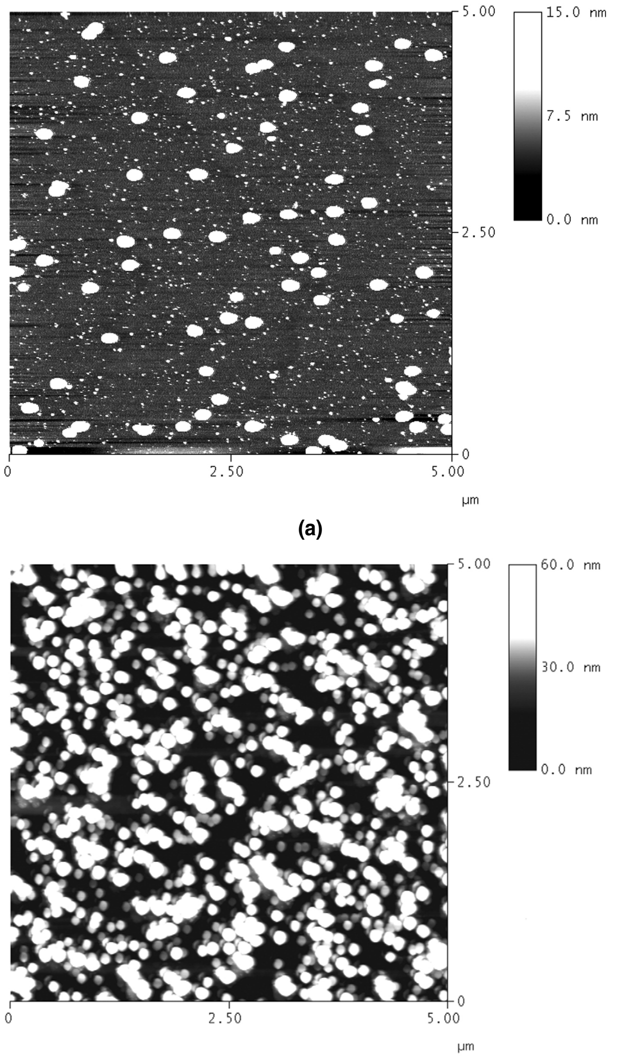
(a)

(b)

Figure 2. AFM (1 x 1 µm) images of Ge-QD deposited under the sample conditions with the following nucleation pressures: (a) 2 Torr, Ge-QD density = $1.3x10^9$ Ge-QD/cm^2, and (b) 5 Torr, Ge-QD density = $3.5x10^{10}$ Ge-QD/cm^2. The mean sizes are equal to 156 nm and 14 nm, respectively.

stant (600° C/20 sccm SiH_4/20 sec.) the Ge-QD density increases 27X compared to the sample analyzed in Figure 2(a), and that the mean size is of 14 nm, thus 11X smaller. It is known that at high total pressures, the SiH_4 concentration on silicon oxide surface is too high, therefore, this phenomenon is likely to be the cause of the promotion of the larger number of Si nuclei.

Figure 3 shows AFM images of Ge-QD samples grown at different SiH_4 gas flow. These images show that decreasing SiH_4 flow from 20 sccm to 10 sccm, the Ge-QD density is increased by 28X and the mean size reduced by 14X compared to the samples obtained at 20 sccm of SiH_4 flow. This set of parameters (600° C/2 Torr/10 sccm SiH_4/20 sec.) leads to the highest Ge-QD density of $3.6x10^{10}cm^{-2}$ and the smallest mean sizes of approximately 11 nm.



(a)

(b)

Figure 3. AFM (5 x 5 μm) images of Ge-QD deposited under the sample conditions with the following nucleation flows: (a) 10 sccm, Ge-QD density = $3.6x10^{10}$ Ge-QD/cm^2, and (b) 20 sccm, Ge-QD density = $1.3x10^9$ Ge-QD/cm^2. The mean sizes are equal to 11 nm and 156 nm, respectively.

Figure 4 shows statistical results of the Ge-QD density and sizes of the samples analyzed in Figure 3. In this graphic one can observe that decreasing SiH_4 flow below 20 sccm, the density of Ge-QD grown on Si nuclei increases abruptly and their sizes are also abruptly reduced. This change on Ge-QD growth behavior can be due to the second step of our process, deposition of Ge, since nuclei may have formed also on SiO_2 [14] from GeH_4 decomposition, due to the smaller density of Si nuclei observed for low SiH_4 flow, however, the combination of theses two effects leads to the increasing of the Ge-QD grown on Si nuclei.

Figure 5 shows an HRTEM image of a Ge-QD prepared with 550° C/5 Torr/40 sccm SiH_4 nucleation conditions. This result evidences the growth of the Ge-QD by LPCVD, and exhibit a typical hemi-

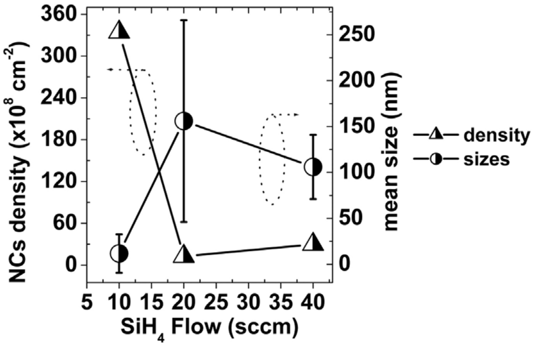


Figure 4. Variation of the density and size of Ge-QD grown on SiO_2 with the SiH_4 flow, for the samples analyzed in Figure 3.

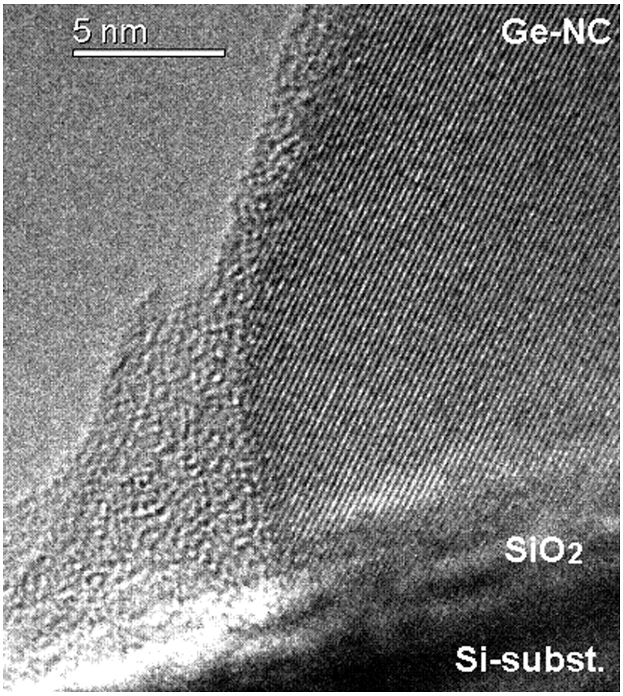


Figure 5. Cross-sectional of HRTEM image of Ge-QD grows on SiO_2. Ge-QD were formed at 550° C/5 Torr/40 sccm SiH_4.

spherical geometry. From this figure one can also clearly observe that the QD present a crystalline order.

Results of Raman spectroscopy characterizations of these samples (not presented in this paper), have shown a well defined characteristic peak around 300 cm^{-1} [15], which is a typical frequency that characterize the Ge crystalline formation. We are confident therefore, that the obtained dots on our samples are of Ge and crystalline.

4. CONCLUSIONS

Define We have studied the influence of nucleation parameters (temperature, total pressure and silane flow) on the density and sizes of Ge-QD on SiO_2. At particular processes conditions, an abrupt increase of Ge-QD density was found to occur as the SiH_4 gas flow is reduced below 20 sccm. The highest Ge-QD density obtained was $3.6x10^{10}$ cm^{-2} with medium size of 11 nm. HRTEM characterization confirmed the formation of quantum dots with crystalline structure which are obtained with no need for high temperature annealing.

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