TIME DEPOSITION DEPENDENT SURFACE MORPHOLOGY AND PHOTOLUMINESCENCE OF Ge NANOISLANDS

ALIREZA SAMAVATI*, ZULKAFLI OTHAMAN,
SIB KRISHNA GHOSHAL[a*]
Ibn Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia, 81310 Skudai Johor Baharu, Malaysia
[a]*Advanced Optical Material Research Group, Department of Physics, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia*

Ge/Si nanoislands having width lies between ~ 55 nm to 85 nm and the height ranges from ~ 6 nm to ~ 21 nm are fabricated using radio frequency (RF) magnetron sputtering deposition technique. The growth kinetics, surface morphology and optical behavior of Ge islands are characterized employing energy dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM) and photoluminescence (PL). The occurrence of the photoluminescence peaks at around 3.29 and 2.85 eV are interpreted to Ge islands and Ge-O interface reaction. The red shift (0.28 eV) for the PL peak position that occurs with changing the islands size is attributed to the effect of quantum confinement. The RMS roughness and number density of islands found to be strongly influenced by deposition time. The minimum of RMS roughness and the maximum of the number density occurred for deposition time 300 sec and 180 sec respectively. The mechanism of size variation of Ge islands with deposition time is analyzed and understood.

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1. Introduction

The novel means of developing new electronic and optoelectronic devices is by nanostructuring of semiconductors. In particular, the discovery of room-temperature visible PL from Si and Ge nanostructures has stimulated much interest in these particular kinds of nanomaterials and in small semiconductor particles. The possibility of tuning the optical response of Ge nanomaterials by modifying their size has become one of the most challenging aspects of recent semiconductor research. Ge/Si heterostructure is suitable for investigating the growth morphology in two and three dimension growth process of Stranski-Krastanov. Ge nanostructure on Si substrate attracted considerable attention due to the possibility of optoelectronic application. Optical properties of these heterostructured islands can be change by changing the islands size distribution [1].

In recent years an intensive research is dedicated towards the growth and optoelectronic characterization of Ge nanoislands on Si substrate employing various deposition conditions for optimization and functionality. The most commonly used fabrication techniques are molecular beam epitaxy [2-4], chemical vapor deposition [5] and thermal evaporation [6]. However, the economical and safer deposition techniques such as radio frequency (RF) and direct current (DC) magnetron sputtering are also exploited for large scale production of Ge nanoislands [7]. Huang et al prepared the Ge\Si nanomultilayer by Magnetron sputtering and determined the crystalline nature of the film at deposition temperature 300 ^oC. A strong agglomeration and the formation of Ge nanocrystals are observed for the samples annealed beyond 800 ^oC [8]. Simonsen et al produced the Ge nanoparticle on Si(001) using electron beam evaporation in which the height

*Corresponding authors: alireza.samavati@yahoo.com

distribution diagram found to be Gaussian and FWHM is increased with increasing island size [9]. It has been observed in the literature that the Ge and GeO_2 nanocrystals luminescence around 3.1 eV and strongest PL intensity was observed for larger nanocrystals [10]. The PL spectra of Ge nanoparticle having size between 2 and 9 nm can be viewed as a combination of three peaks at around 1.9, 2.3 and 3.0 eV as reported by Kartopu et al [11]. The Ge islands having height from 1 to 2 nm and widths from 40 to 50 nm are fabricated by Thanh et al in which the observed broadening in the PL spectra are correlated to the broad dispersion in the quantum size distribution [12]. Fahim et al reported the growth of Ge nanoparticle islands having size between 8 nm to 20 nm grown by electron beam evaporation method where the strong sensitiveness of RMS roughness on annealing temperature is confirmed. Furthermore, the thermal annealing found to affect substantially the structural, optical (0.25 eV shift for band gap energy due to changing the particle size) and electrical properties of Ge thin films [1].

The visible luminescence from Ge nanoparticles and nanocrystallites generated interest due to the feasibility of tuning band gap by controlling their sizes. However, controlling the light emitting behavior require careful fabrication of such nanostructure. In this work, the radio frequency magnetron sputtering is chosen to deposit Ge/Si islands. The structures and properties of Ge islands are studied by changing the deposition time from 180 sec to 420 sec. Despite of few studies the role of deposition time on the formation of Ge islands is not clearly understood. The focused objectives of this study are to better understand the role of time deposition on the structure, surface morphology and optical behavior of Ge nanoislands with pyramid-shape structures. Different characterization techniques such as AFM, EDX and PL are employed. The results for the RMS roughness, number density and PL intensity as a function of deposition time are presented and explained.

2. Experimental

RF magnetron sputtering (HVC Penta Vacuum) is used to prepare a series of Ge nanoislands on Si(100) substrate. Single crystal Ge (99.99 %) with a diameter of 3 inch is employed as sputtering target. The substrate is rinsed to deionized water and dry with N_2 prior to the placement in the chamber. Weak Hydro Fluoric acid (HF ~ 5 %) is employed to remove the oxide layers from the substrate surface and then by Ultrasonic at room temperature for 20 min. The base pressure in the vacuum chamber is less than 8×10^{-6} mbar and the working gas (Ar) is injected in the chamber and the pressure is maintained at pressure 6.5×10^{-3} mbar. Before deposition, the samples and chamber are cleaned by ion radiation for 2 min. During deposition process, 300 ^{0}C substrate temperature, 100 W RF power and 10 Sccm Ar flow are applied. Throughout growing, the turbo pump was working in order to achieve the lower pressure. The islands are grown in different deposition time, 180 sec (sample A), 240 sec (sample B), 300 sec (sample C) and 420 sec (sample D). These samples are now subjected to structural characterization. The sizes, density and RMS roughness of islands are measured with AFM operating in contact mode. The elemental analysis is carried out using EDX. The PL spectra are recorded under 239 nm excitation with an argon ion laser. All the measurements are performed at room temperature.

3. Results and discussions

The EDX spectrum for samples A and D in figs. 1a and b respectively suggest the presence of Ge on the Si surface. The presence of oxygen peak is due to the formation of

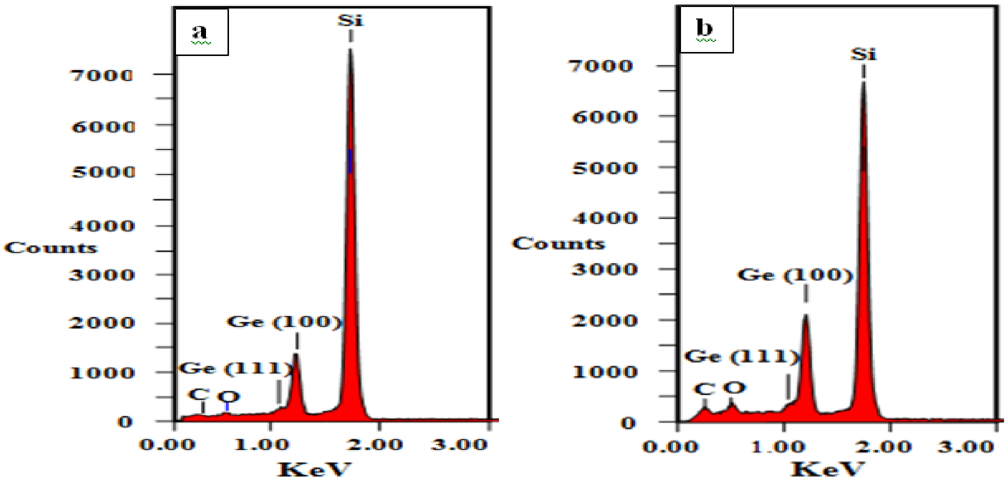

Fig. 1 EDX spectra of Sample A (a) and D (b)

GeO_x complex resulting from surface passivation effect on Ge nanoisland. Interestingly the intensity of Ge peak is prominent and for sample D is more stronger than sample A which is due to the existence of larger size Ge islands along (100) direction. A weak peak for Ge is attributed to the growth of Ge crystals along the (111) direction.

Figures 2a, b, c and d represent the AFM image in two dimensions for the surface morphology of samples A, B, C and D respectively. The formation of Ge islands is clearly evidenced. The oscillation associated with the height distribution of the line scans (indicated as black line) over 500 nm in figs. 2i. j, k and l clearly illustrate the height fluctuation and the size variation of Ge islands for samples A, B,C and D respectively. Furtheremore , these figures also exhibit a kind of pyramidal structure of Ge islands located on the surface. The fluctuation of heights of Ge islands is more apparent in three-dimensional atomic force micrograph (figs. 1e, f, g and h) and in the height distribution as summarized in Table. 1. The AFM images clearly illustrate the existence of Ge islands having heights between 6 nm (sample C) to 21 nm (sample B) and width between 50 nm (sample A) to 85 nm (sample D). The trend of height fluctuation with increasing deposition time can be explained using the Stranski-Krastanov (S-K) growth mechanism. In the S-K process the islands after forming the wetting layer nucleates as three dimensional square shaped pyramid structures of Ge islands [13, 14]. These pyramidal structures transform to larger multifaceted pyramid-shape islands (figs. 1f and j) by further increase of deposited material and collection of more adatoms from the neighboring islands following the coarsening process called Ostwald ripening. A large number of relatively smaller islands shrink irrespective of their size and eventually disappear with continual Ge deposition over the Si surface covered with Ge islands as evidenced from figs. 1g and k [15]. This kind of structural change in achieving the minimally stable free energy configuration of the morphology may be understood by using the theory of self organized criticality. Additionally, the quantum size effect become less prominent with decreasing the number densities and gets reflected in the islands distribution as indicated in fig. 1g. Finally, the increase of deposition time to 420 sec leads the islands structure to evolve in a configuration where a relatively stable and steady state distribution with large sized islands distribution is achieved as depicted in fig. 1h and l.

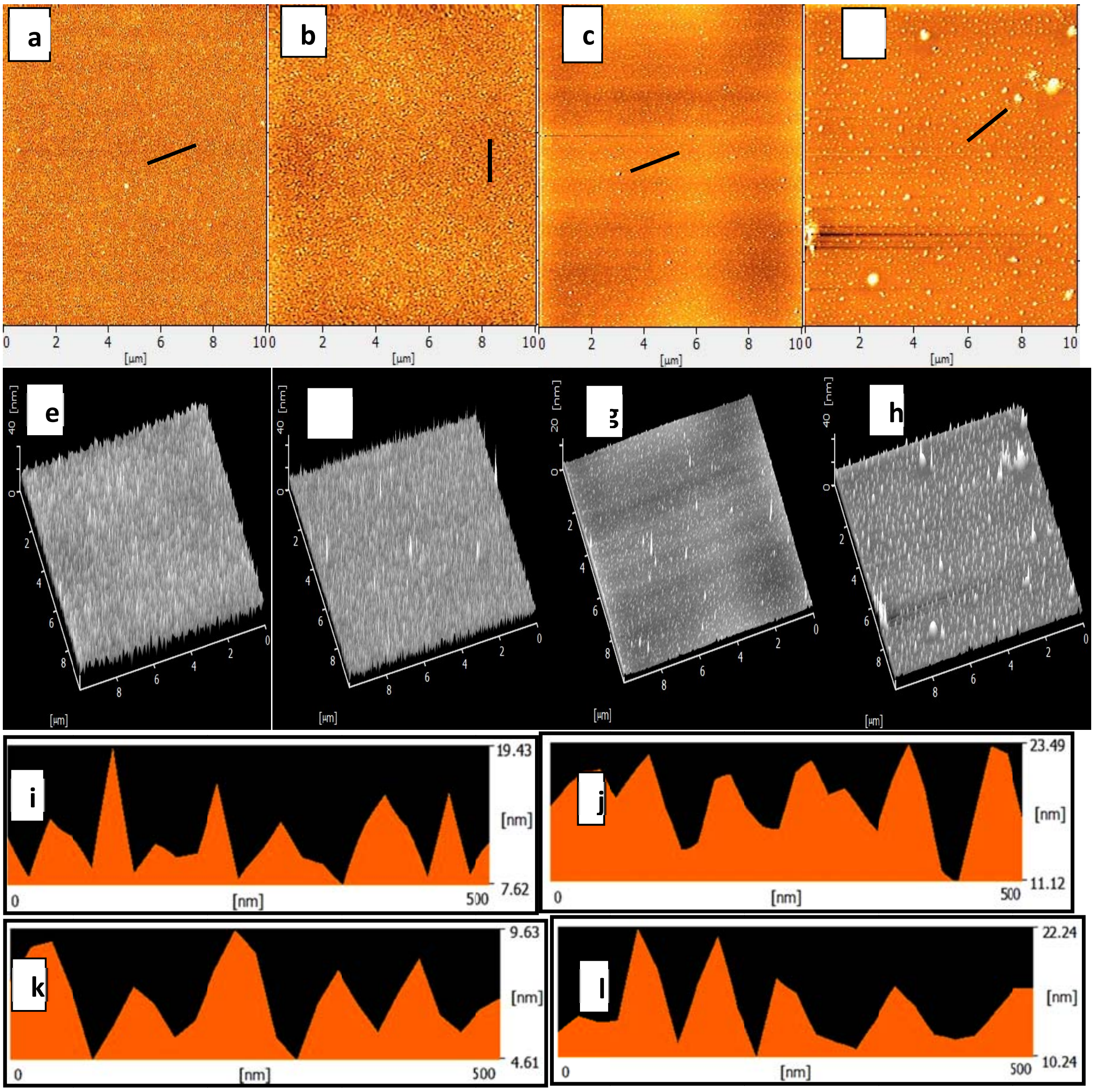

Fig.1. Two – dimensional AFM images of sample A(a), B(b), C(c) and D(d), 3D AFM images of samples A(e), B(f), C(g) and D(h), Height fluctuation of samples A(i), B(j), C(k) and D(l)

At a higher time deposition, the Ge adatoms will diffuse to a longer distance at surface and prefer to condense into a pre-nucleated islands having lower activation energy, rather than produce a new nucleation center that requires higher energy for activation. These competitive processes lead to the development of larger Ge islands resulting lower number density (Table 1).

The RMS roughness is a measure of the surface quality which eventually decides the optical properties of the islands [1]. Variation of RMS roughness as a function of deposition time is shown in table. 1. The RMS roughness shows a monotonic decrement as deposition time is further increased from sample B to C. The minimum RMS roughness that is obtained for sample C with deposition time of 300 sec is attributed to the formation of homogenous islands with similar size and smallest height evolving towards more stable states. The variation in the value of RMS roughness is directly correlated to the island height distribution as indicated in table. 1. The number density drops drastically after 240 sec deposition time and saturates beyond this time (table. 1). A maximum density of 9×10^{9} cm^{-2} with average width of 55 nm are obtained for sample

A. The trend of rapid decrement in the density distribution as a function of the deposition time or increment of the islands size can be understood by the deposition time driven growth processes.

Table 1. The deposition time dependent average width, average height, number density, RMS roughness, PL peak intensity and band gap energy.

Deposition Time (sec)	Average Width (nm)	Average Height (nm)	Number Density $\times 10^9$ cm^{-2}	RMS Roughness (nm)	PL Peak Intensity (a.u.)	Band Gap Energy (eV)
180	55	13	9.0	2.9	900	3.29
240	66	21	4.5	3.7	700	3.22
300	68	6	3.5	0.9	550	3.20
420	85	11	3.5	1.5	550	3.01

The room temperature visible PL and the shift in the band gap energy of Ge nanoparticles are intensively studied [16, 17]. The PL spectra of Ge(O) are shown in fig. 4. The intense peaks at 3.29, 3.22, 3.20 and 3.01 eV corresponds to samples A, B, C and D respectively. Different peak positions are related to the formation of different Ge island sizes. The constant shift in the PL peak position towards the lower band gap energy with increasing islands size (from A to D) confirms the effect of quantum confinement. However, the change in the band gap energy ~ 0.02 eV between samples B and C is relatively lower due to their small size variation as can be seen from table 1. Appearance of weak peaks at around 2.85 eV for samples B and C is related to the Ge and GeO_X interface reaction [18, 19] that become less likely for both, very small and very large islands as appeared in sample A and D respectively. The peaks that occurred at higher energy (~ 4.14 eV) are probably related to the existence of nanoislands of different symmetries, shapes and sizes. More generally, the appearance of the peaks might have emerged from the photo-generated charge carriers trapped in the shallow

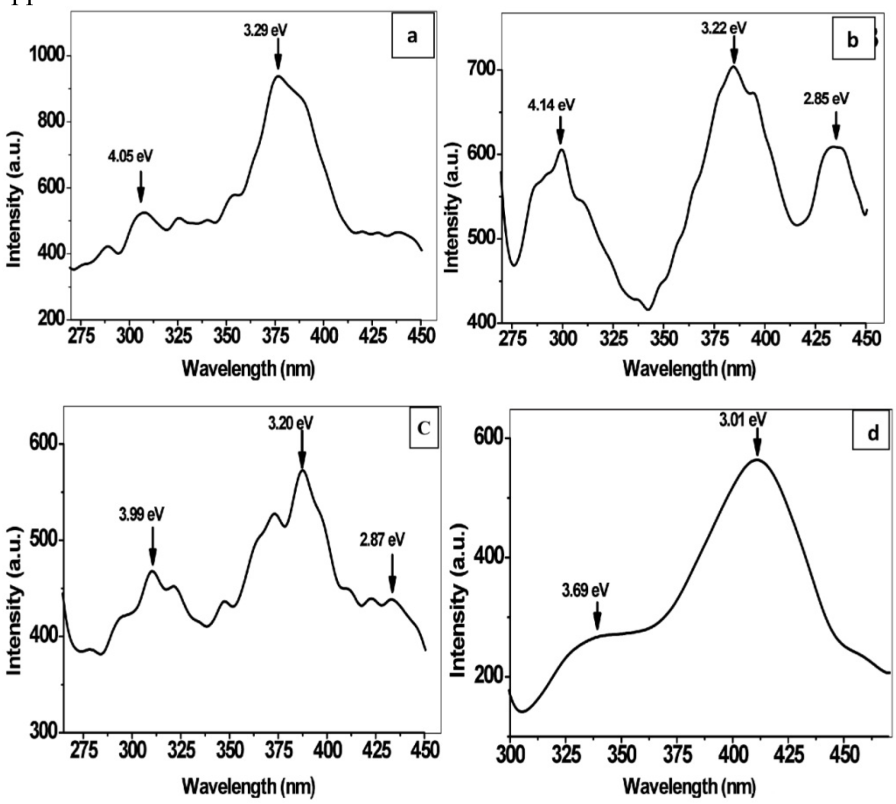

Fig. 4 PL spectra of samples A (a), B (b), C (c) and D (d)

states that are tunneled to recombine. The emission from carrier recombination in shallow traps (sample D) appears at lower wavelength than deep traps (sample A). The broad emission band represents the superposition of wide distribution of trap distances [20]. In our experiment, the maximum PL intensity is achieved for the sample A having high density. However, the origin of the decreasing nature of the PL intensity with increasing the deposition time is related to the number density of the islands.

4. Conclusion

The RF magnetron sputtering technique is used for the fabrication of Ge nanoislands on Si substrate at 300 ^{O}C substrate temperature at different time of deposition. The influence of deposition time on growth morphology such as the number density, the width and the height distribution, the RMS roughness and PL spectra are examined and compared with other findings. The AFM images clearly indicate the role of deposition time on the growth process of the island structures and size distribution (~ 55 to ~ 85 nm width and ~ 6 to ~ 21 nm height) of Ge islands. The EDX spectra confirm the formation of Ge islands and indicate the interface reaction between Ge and GeO_2. The mechanism behind the deposition time dependent variation of the size distribution and roughness fluctuation are analyzed and understood. The number density and the island size are found to be very sensitive to the variation of deposition time during the growth process. The room temperature PL spectra of the Ge/GeO_x show the strong dependence on the deposition time as observed in the shift of PL peak position, peak intensity and broadening. The shift in the island size dependent PL peak position from 3.29 to 3.01 eV confirms the effect of quantum confinement. The RF sputtering technique is not only economic but also suitable for easy preparation of high density nanoislands (configuration of Ge islands at deposition temperature 300 ^{o}C and ambient pressure 6.5×10^{-3} Torr) compared to the expensive and complex MBE and CVD methods.

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