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# Synthesis of ultra-small Si/Ge semiconductor nano-particles using electrochemistry

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ABSTRACT

In this paper, we describe the formation of colloidal Si/Ge semiconductor nano-particles by electrochemical etching of Ge quantum dots (GEDOT), Silicon–Germanium graded layers (GRADE) and Silicon–Germanium multi-quantum well (MQW) structures which are prepared on Silicon wafers using low pressure chemical vapor deposition (LPCVD) technique. The formation of Si/Ge nano-particles is verified by transmission electron microscope (TEM) images and photoluminescence (PL) measurements. The Si/Ge nano-particles obtained from GEDOT and GRADE structures, gave blue emissions, upon 250 nm, and 300 nm UV excitations. However, the nano-particles obtained from the MQW structure did exhibit various color emissions (orange, blue, green and red) upon excitation with 250 nm, 360 nm, 380 nm and 400 nm wavelength light.



## 1. Introduction

There has been a great interest in semiconductor nano-particles in recent years, due to their strong visible photoluminescence. It is known that Si nano-particles [1] and Ge nano-particles [2] do exhibit visible PL emissions upon UV illumination. Semiconductor (Si, Ge) nano-particles are used to tune the optical properties of opto-electronic devices. Researchers used such nano-particles to improve the performance of solar cells [3]. Efficient ultraviolet photodetectors [4], and metal-oxide-semiconductor (MOS) memory devices [5], have been developed and reported in the literature using these nano-particles. Since the early 1970s, researchers were also interested in SiGe alloys because their band gaps are variable between bulk Si and Ge via the so called "band structure engineering" [6]. It is known that SiGe alloy is compatible with Si technology and is used in monolithic integrated devices for optical communication wavelengths [7,8].

It is possible to obtain Si/Ge nano-particles using many methods such as, thermal evaporation [9], chemical vapor deposition [10], laser ablation [11], and magnetron co-sputtering [12]. Researchers report that, PL intensity peak frequencies depend on nano-particle size due to phonon confinement, strain and nano-crystal composition [12]. Adriaenssens et al. [13] prepared Si/Ge co-sputtered films and his team observed strong blue emissions (around 440 nm) upon excitation with 260 nm, 300 nm and 360 nm light source. The emissions were a result of Si/Ge nano-crystal formation upon thermal annealing. Ong et al. [14] did obtain Si/Ge nano-crystals in thin film form using pulsed laser ablation and then thermal annealing. They discovered that, 280 nm excitation gave PL emission around 400 nm which is similar to pure Silicon nano-crystals in $Al_2O_3$ films. However, 380 nm excitation gave a PL spectrum which is similar to pure Ge nano-crystals in $Al_2O_3$ films. These research results showed the formation of Si/Ge nano-particles in thin solid forms.

A recent technique, reported by Nayfeh [15,16], is a high throughput and low cost method for producing semiconductor (Silicon) nano-particles with an average diameter of 1 nm, in solution form. This method is based on electrochemically etching bulk Silicon wafers using a mixture of hydrofluoric acid (HF), hydrogen peroxide ($H_2O_2$) and methanol. Upon electrochemical etching, Silicon wafer becomes porous followed by the collection of

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Silicon nano-particles from the surface by ultrasonic treatment. The resulting ultra-small particles give bright blue luminescence upon UV light illlumination [16]. They also showed that, it is possible to obtain ultra-small Germanium nano-particles [17] through similar anodization process. These nano-particles emit blue, green and yellow (orange) light with 365 nm excitation. Kimura et al. [2] used a different technique and obtained Ge nano-particles with an average size of 3.1 nm. They did report that organic molecule terminated Ge nano-particles emit blue light but hydrogen terminated Ge nano-particles emit red light upon UV illumination.

Inspired by these research results, we did obtain Silicon/Germanium (Si/Ge) semiconductor nano-particles through a similar electrochemical etching using (LPCVD grown) Ge quantum dot (GEDOT), Si/Ge graded layer (GRADE), and Si/Ge Multi-Quantum Well (MQW) films on Silicon wafers. These three different starting materials are chosen in order to see the effect of different initial Ge content on the formation of ultra-small Si/Ge nano-particles in solution form. In this work, we explain the method for producing these ultra-small nano-particles and nano-particle photoluminescence properties. Transmission Electron Microscopy (TEM) study also confirmed the growth and distribution of these ultra-small semiconductor (Si/Ge) nano-particles.

## 2. Experimental

### 2.1. Multi-quantum well (MQW) thin film growth

The ultra thin alternating layers of Ge and $Si_{1-x}Ge_x$ were grown by a recently developed heteroepitaxy technique [18]. Single crystal Boron-doped (100) Silicon wafers were used as starting substrates. Wafers were treated by standard organic (RCA1) and metal (RCA2) cleans followed by immediately loading into epitaxial reactor. The samples were annealed in $H_2$ ambient, at 0.106 bar pressure, at 1000 °C for 5 min to obtain an epitaxy-ready surface free of any native oxides. Heteroepitaxial growth of Ge directly on Silicon was hampered by 4.2% lattice mismatch resulting in defects and threading dislocations. A thin layer of (370 nm) Ge was grown at 400 °C followed by annealing at 825 °C for 20 min, in $H_2$ ambient. Surface reconstruction by enhanced diffusion and dislocation annealing provided a smooth Ge layer with reduced defect density [18,19], resulting in a Ge crystal template. Ten pairs of bi-layers of 100% Ge (10 nm) and $Si_{0.1}Ge_{0.9}$ (20 nm) were grown on the virtual Ge substrate at 400 °C with $SiH_4$ and $GeH_4$ gas mixtures. No doping species were introduced during the growth of the alternating multilayer. In order to avoid any interdiffusion of Si and Ge, and the diffusion of doping species from highly doped regions, no intermediate annealing steps were performed. A 100-nm thick Ge-rich cap layer was grown on the top.

### 2.2. Germanium quantum dot (GEDOT) thin film growth

GEDOT films were grown on Si wafers after similar cleaning and surface preparation as explained above. The native oxide on Si surface was removed by hydrogen baking and an ultra thin Si epitaxial layer was grown. The growth temperature was then set to 400 °C for Ge NC formation. The growth time, process pressure and the gas flows were varied to obtain various size nano-crystals. Thin Ge layers incubated and grew in an island fashion before coalescence. Silicon cap layers were deposited before coalescence. Thus, Ge nano-crystal layers were left sandwiched in Si matrix.

### 2.3. Si/Ge grade layer (GRADE) thin film growth

GRADE layer was grown on Si wafer by varying $SiH_4$:$GeH_4$ mixture ratios. A 100% Ge buffer layer (500 nm) was initially grown on Si followed by gradual increase in $SiH_4$:$GeH_4$ ratio. Grading was semi-continuous from Ge:Si ratio from 10:0 to 6:4 over 500 nm film thickness. The ratio was changed to 4:6 for 100 nm film and 100% Si was deposited for 100 nm.

### 2.4. Si/Ge nano-particle synthesis and characterization

We did obtain Si/Ge nano-particles through anodization of the thin film structures (GEDOT, GRADE and MQW) in a mixture of $H_2O_2$/HF and methanol. We used a standard Keithley 2400 sourcemeter to maintain constant current (1–20 mA $cm^{-2}$) in the etching setup. After 6–7 h etching, the wafers were transferred into glass vials filled with de-ionized (DI) water. The solutions were sonificated and the large particles were filtered out using commercial 100 nm filter papers (Minisart High-Flow, 16553).

The Si/Ge nano-particles were drop-casted on Cu grids from the solution and TEM images of these particles were taken using FEI Technai, G2 F30 type of electron microscope. The PL emissions were recorded with a VARIAN (Cary Eclipse) spectro-fluorometer instrument and attenuating mirrors (2.5%) were used to avoid saturation of the detector. The XPS spectrum was obtained using a THERMO monochromated High-Performance XPS spectrometer equipped with an Al K Alpha source and standard lenses. The measurements were done with an acquisition time of 4 s and a spot size of 400 μm.

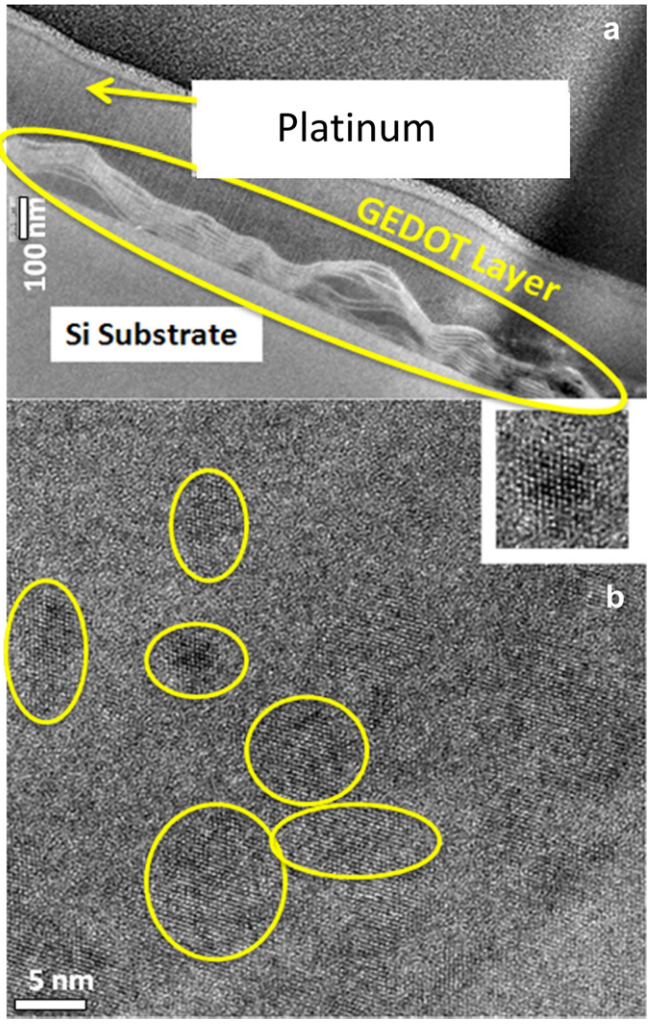


**Fig. 1.** (a) Low magnification TEM image of the GEDOT sample (scale bar: 100 nm). (b) Quantum dots shown in high magnification (scale bar: 5 nm).

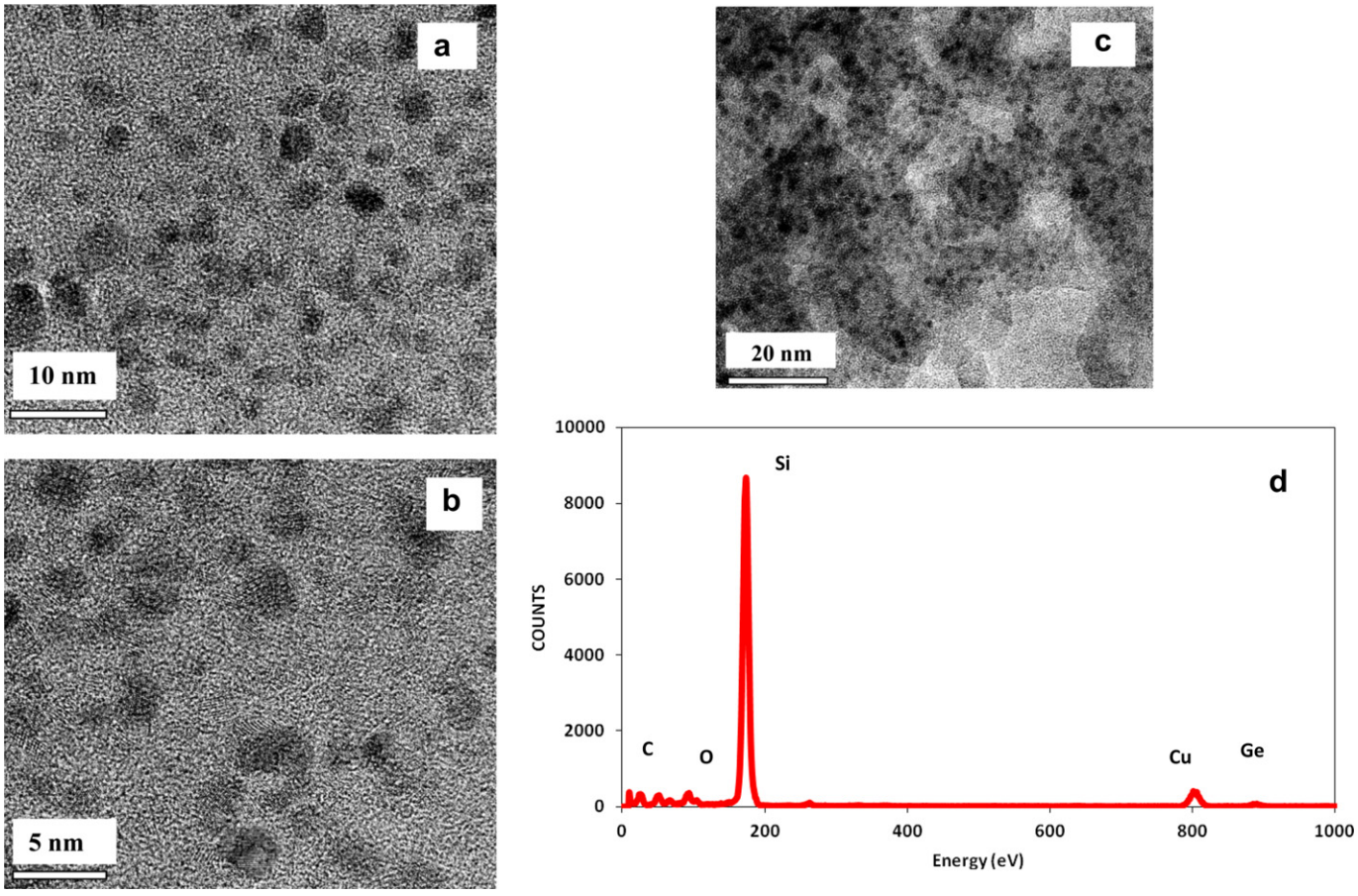


**Fig. 2.** TEM image, Si/Ge nano-particles (a), (b), (c), EDAX data Si/Ge nano-particles (d).

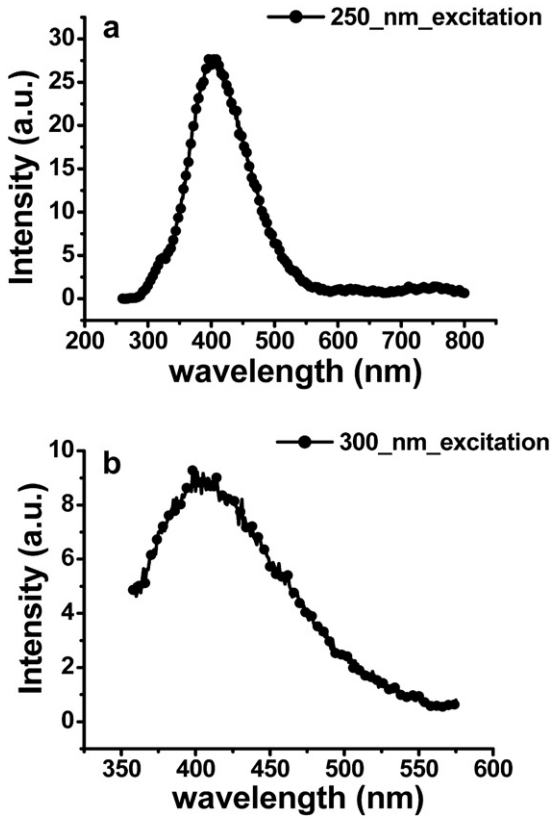


**Fig. 3.** (a) PL emission, upon 250 nm excitation, 2.5% attenuator was used. (b) PL emission, upon 300 nm excitation, 2.5% attenuator was used.

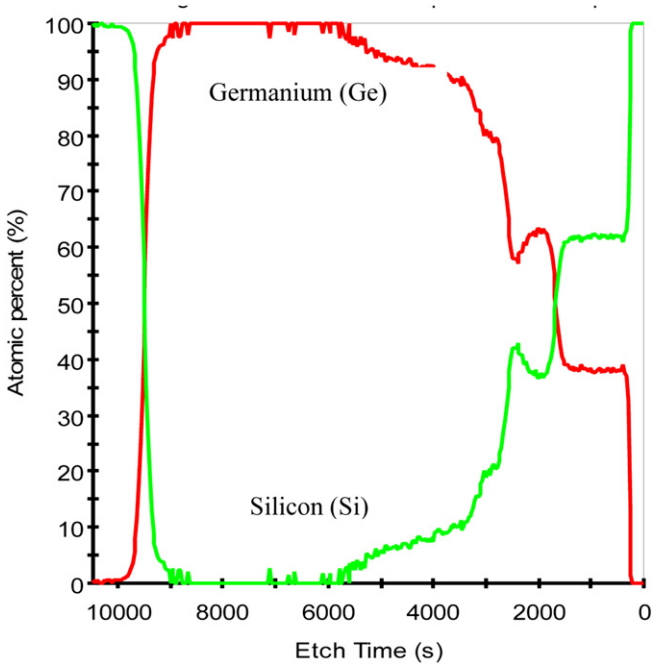


**Fig. 4.** XPS atomic percent profile, etching parameters: high current, etch rate: 0.5 nm $min^{-1}$, etch time 4 h.

## 3. Results and discussions

### 3.1. Nano-particles obtained from Ge quantum dots (GEDOT) on Silicon

Fig. 1 shows the TEM image of the initial GEDOT structure which was grown on *p*-type Silicon (100) substrate. Germanium island formation on Silicon substrate could be seen in the TEM image. Ge-islands have a wide size distribution which is not attempted to be quantified. We did not study the effect of Ge-islands size distribution on the formation of ultra-small semiconductor nano-particles.

Electrochemical anodization process produced ultra-small semiconductor nano-particles inside the solution. TEM images confirm the formation of these ultra-small semiconductor nano-particles (Fig. 2a–c). The average size of the nano-particles are 1–3 nm, obtained from the TEM images.

It is know from the literature that, electrochemical etching process produces a family of semiconductor nano-particles with average size of 1–3 nm and these ultra-small semiconductor nano-particles give size-dependent PL emissions due to quantum confinement effects [17,20]. Nayfeh reported that, 1 nm size nano-particles emit blue, 1.67 nm size particles emit green, 2.15 nm size particles emit yellow/orange, 2.9 nm size nano-particles emit red and 3.7 nm size particles emit infrared light upon UV illumination [17,20]. It is also known that, larger size semiconductor nano-particles give emissions upon longer wavelength excitations due to different band gap values.

Upon excitation with 250 nm and 300 nm wavelength light, nano-particles that we obtained gave blue emissions centered around 402 nm and 403 nm (Fig. 3a, b). A 2.5% attenuator was used during the PL measurements. The light absorbance is maximum at 250 nm excitation and the broadest PL emission is observed at 300 nm excitation. Therefore, the PL emissions at these wavelength excitations are reported in this paper. We think that, broadening of the PL emission is due to less amount of light which is being absorbed at higher wavelength excitations.

These PL emissions also verify the formation of ultra-small (1–3 nm) semiconductor nano-particles in solution form and the EDAX (Energy Dispersive X-Ray Analysis) measurements determined an elementary weight percentage of %99.74 Silicon and % 0.26 Germanium, indicating that most of the synthesized nano-particles are Silicon. Therefore we think that, the PL emissions are mostly due to Silicon nano-particles formed inside the solution (Fig. 2d).

### 3.2. Nano-particles obtained from Si/Ge graded layers (GRADE) on Silicon

Fig. 4 shows the XPS (X-ray Photo-Electron Spectroscopy) atomic percent profile of the initial GRADE structure that was

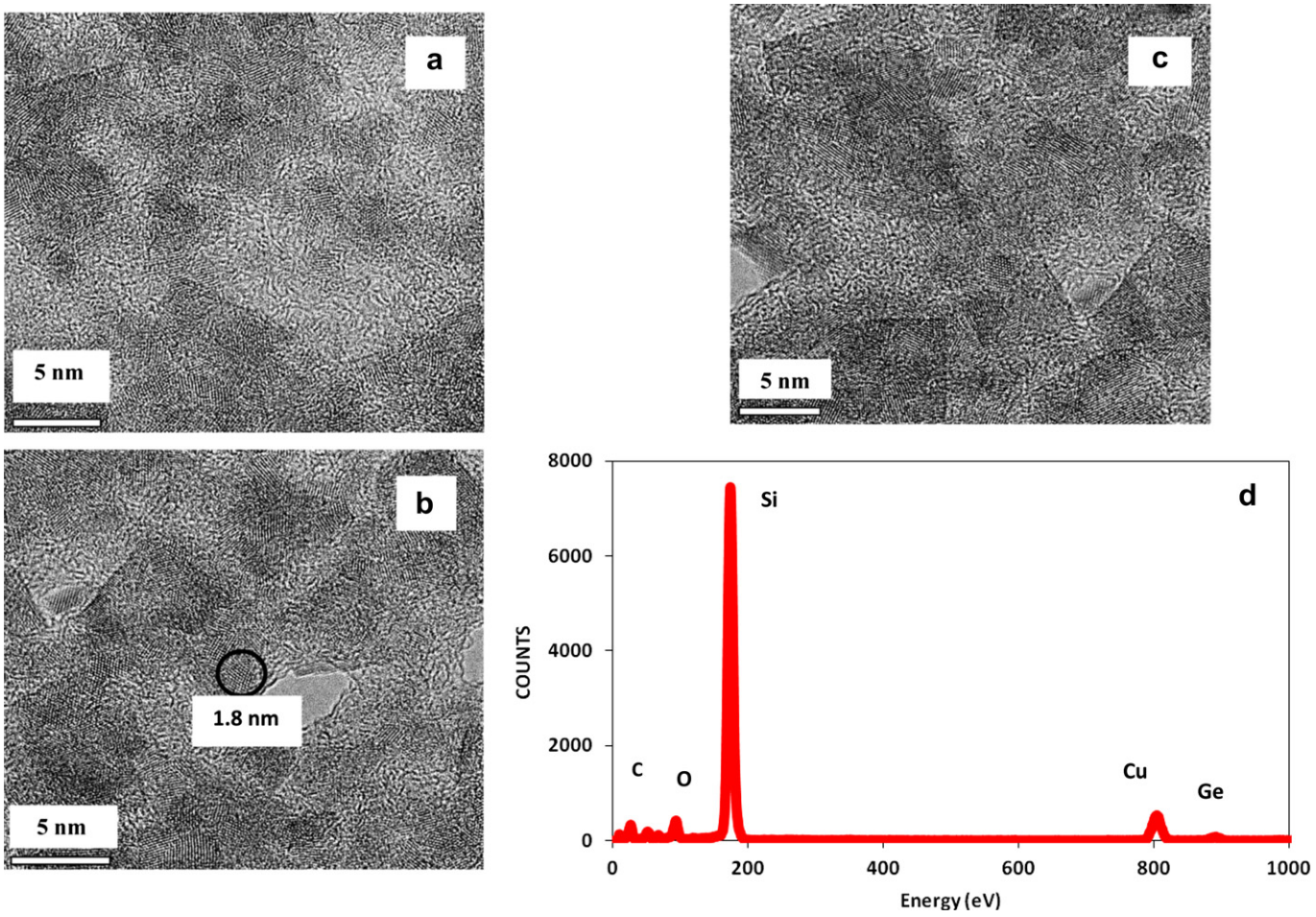


**Fig. 5.** TEM image, Si/Ge nano-particles (a), (b), (c), EDAX data Si/Ge nano-particles (d).

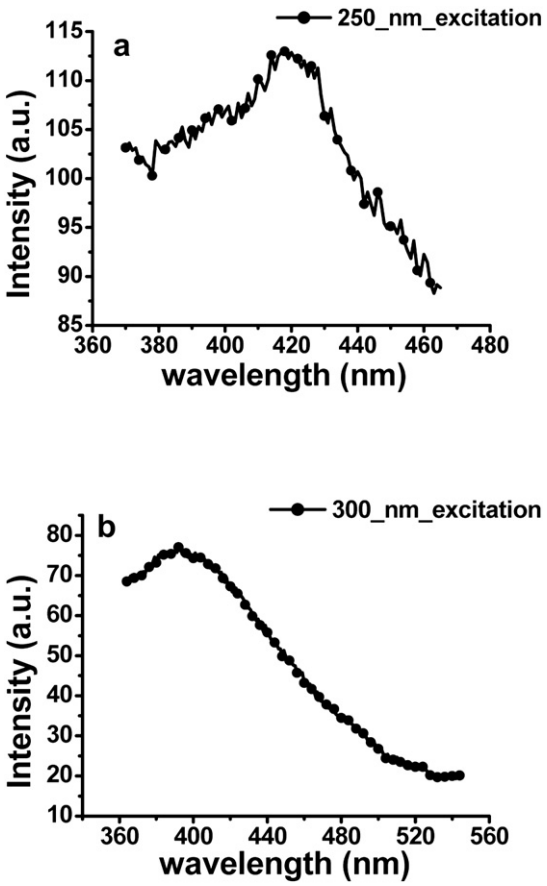


**Fig. 6.** (a) PL emission, upon 250 nm excitation. (b) PL emission, upon 300 nm excitation.

grown on Silicon substrate. This data was obtained with high etching current, with an etch rate of 0.5 nm $min^{-1}$ and the total etch time was 4 h.

XPS data shows that, there is a gradual decrease in Silicon content and an increase in Germanium content with increasing etching time.

After the anodization process, we did obtain ultra-small semiconductor nano-particles and nano-particle formation is verified by the TEM images as shown in Fig. 5a–c. The average particle size as seen from TEM images is again 1–3 nm.

In addition to TEM images, we also report the photoluminescence emissions of these nano-particles upon UV illumination. Fig. 6a, b shows the PL emissions upon UV excitations.

A 250 nm excitation gave blue emission around 418 nm, 300 nm excitation gave broader blue emission around 395 nm. PL emissions also confirm the formation of semiconductor nano-particles in solution form. On the other hand, the EDAX elementary weight composition data shows that there is %99.76 Silicon and %0.24 Germanium in the final solution indicating that the PL emissions are mostly due to Silicon nano-particles (Fig. 5d).

### 3.3. Nano-particles obtained from Si/Ge MQW on Silicon

Prior to the anodization process, we did obtain data about the structural properties of the initial MQW structure. Fig. 7 shows the diagram and the TEM image of the MQW structure that we used in anodization. Ge and SiGe bi-layers are shown in the TEM image.

Ultra-small semiconductor nano-particles were obtained through the electrochemical anodization process. The formation of the nano-particles is verified by TEM images and PL measurements. TEM images of the nano-particles could be seen in Fig. 8a–c and the PL data is given in Fig. 9a–d. Average size of the nano-particles obtained from TEM images, is 1–3 nm.

PL data shows that, 250 nm excitation gave blue (422 nm), green (505 nm) and orange (604 nm) emissions. A 360 nm excitation gave orange (605 nm) emission, 380 nm excitation gave green (516 nm) and red (677 nm) emissions and 400 nm excitation gave green (538 nm) and red (685 nm) emissions. PL measurements were obtained using a 2.5% attenuator in order to get a clear emission spectrum.

EDAX measurements (Fig. 8d) show that Si/Ge weight ratio is 2.7 (%73 Silicon, %27 Germanium). The weight percent difference accounts for the differences in PL spectrum compared to previous two cases. In previous two cases, we only observed blue emissions and based on the EDAX data, we think that these emissions are a result of ultra-small Si nano-particles. However, in this case, we believe that, the blue, green, yellow/orange, red and infrared emissions that we observed are a result of ultra-small (<5 nm) Si/Ge nano-particles formed inside the solution. We also know from the literature that ultra-small Ge nano-particles give blue, green, yellow/orange and red emissions upon UV light illumination [17]. TEM images, the EDAX data and the PL emissions together verify the formation of ultra-small Si/Ge semiconductor nano-particles in solution form.

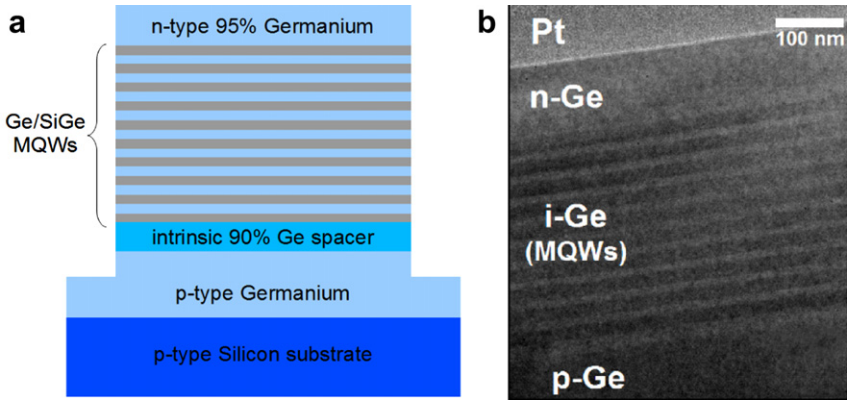


**Fig. 7.** (a) Illustration of the grown stack including alternating multilayer. (b) Cross-sectional TEM image of the heteroepitaxial layer (770 nm) grown on Silicon.

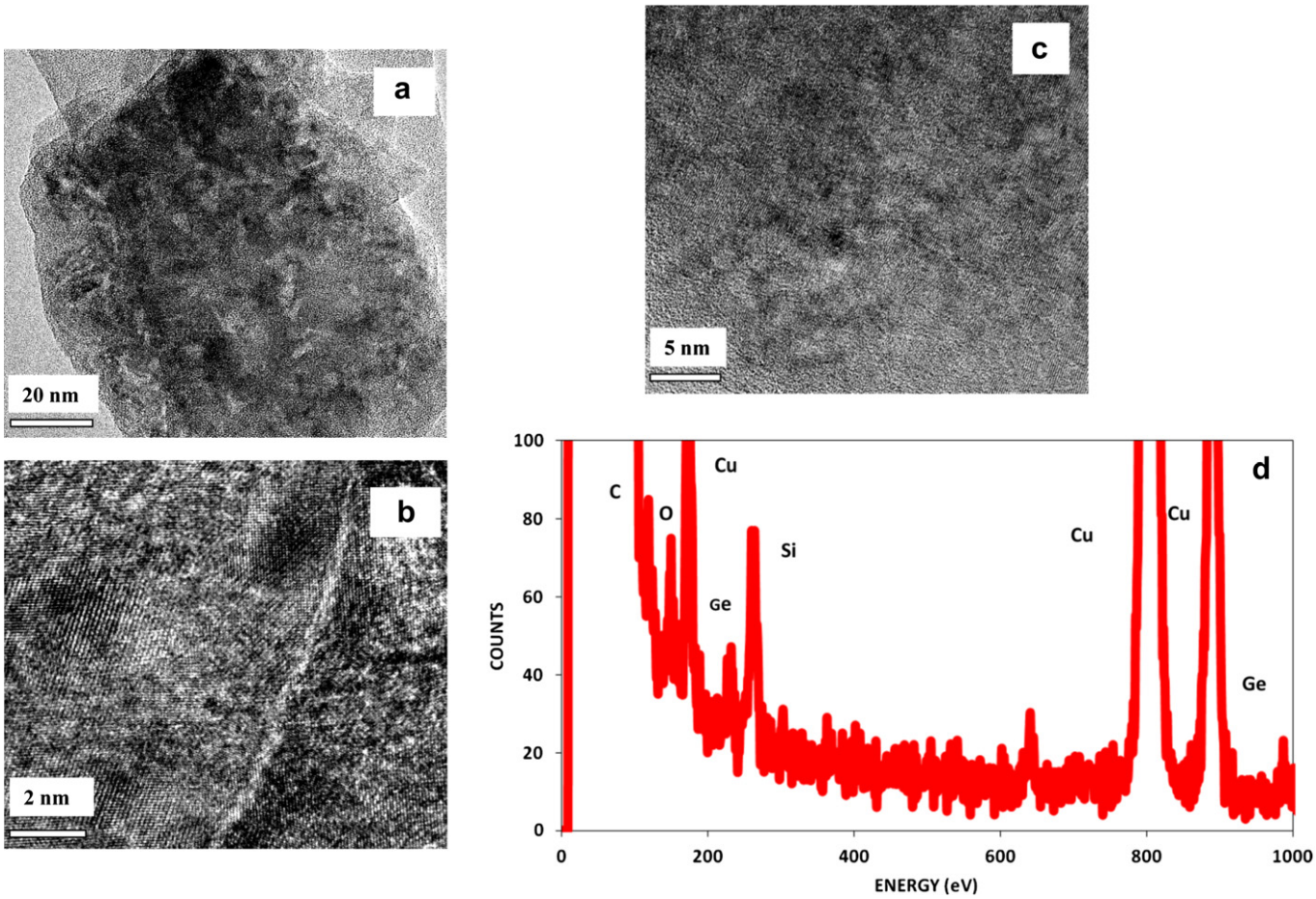


**Fig. 8.** TEM image, Si/Ge nano-particles (a), (b), (c), EDAX data Si/Ge nano-particles (d).

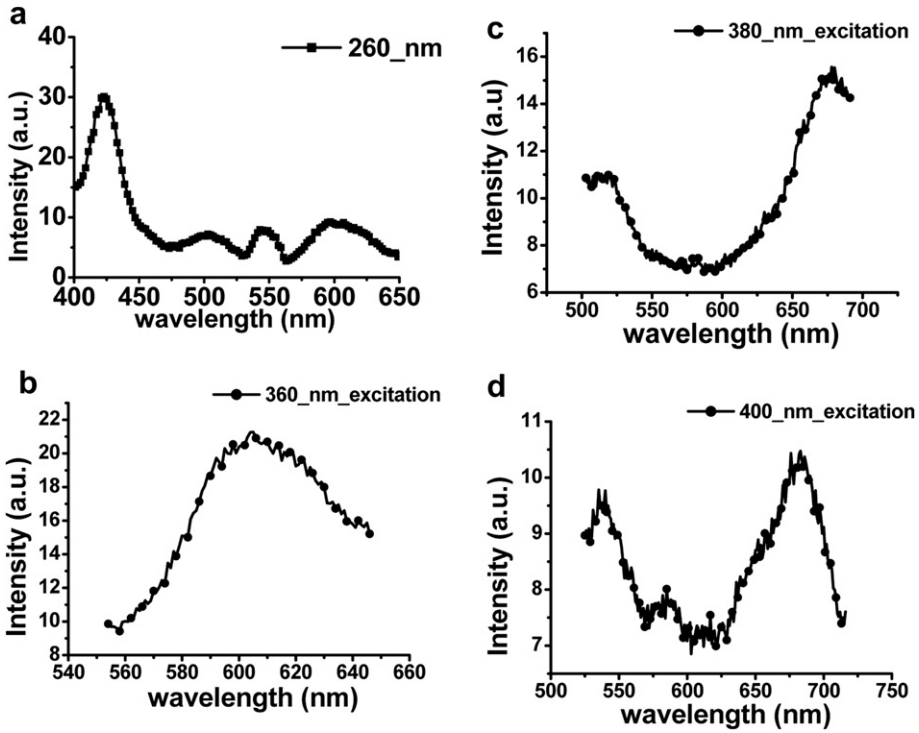


**Fig. 9.** (a) PL emission, upon 250 nm excitation, 2.5% attenuator was used. (b) PL emission, upon 360 nm excitation, 2.5% attenuator was used. (c) PL emission, upon 380 nm excitation, 2.5% attenuator was used. (d) PL emission, upon 400 nm excitation, 2.5% attenuator was used.

## 4. Conclusion

In this paper, we tried to explain the formation of Si/Ge nano-particles through electrochemical etching of Ge quantum dots (GEDOT), Si/Ge graded layers (GRADE) and Si/Ge Multi-Quantum Well (MQW) structures on Silicon. In the first two cases, the failure to synthesize Silicon and Germanium nano-particles together in solution form could be attributed to the low Germanium content in the initial anodized structures. However, the Si/Ge MQW structure had a quite sufficient amount of Germanium that was enough for the synthesis of Si/Ge nano-particles in solution form. Due to high costs of Ge wafers, this one step process could be a low cost and alternative method for producing Si/Ge nano-particles inside the solution. Various color photoluminescence abilities of these Si/Ge nano-particles could make them promising candidates for multi-band opto-electronic device applications.

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