Ge nanostructures doped silica-on-silicon waveguides

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ABSTRACT

Ge nanostructures embedded in silica matrix are emerging as a promising material for new generation devices due to the unique electric and photonic properties. In this paper, Ge nanoclusters and nanocylinders with Ge shell were successfully formed by the high energy electron irradiation in the PECVD deposited glass film. In addition, large area Ge nanoclusters were also created by heat-treatment of PECVD deposited glass film. These nanostructures were characterized in terms of size, composition, distribution and crystalline state by using TEM, HRTEM, EDS, SEM, Raman spectroscopy, and SIMS. Waveguides doped with Ge nanoclusters were fabricated and their absorption has been characterized in a wavelength range from 500nm to 1700nm.

Keywords: Ge nanocluster, nanocylinder, nonlinearity, TEM, Raman spectroscopy, silica-on-silicon waveguide, e-beam irradiation, heat-treatment, silicon photonics

1. INTRODUCTION

One of the most important materials within optical communication, if not the most important is silica (glass). Nearly all optical fibers and planar waveguide components are made using silica due to its extremely low propagation loss at the wavelength band around 1550 nanometers and its extremely stable chemical properties under harsh environments. In addition, silica has also played an important role for the maturity of microelectronics due to its easy growth from a silicon substrate. However, amorphous silica has very low nonlinearity and as a consequence can hardly be used for any active components. Therefore, there is a constant strive to research suitable nonlinear optical material. Recently, a huge amount of investigation and research efforts have been put into silicon photonics all over the world, with the intent of making optical functionalities based on the well-developed CMOS silicon platform and then monolithic integration of both optical components and electronic components on the same silicon substrate.

In comparison with electronic properties of Si, Ge has a larger dielectric constant and smaller effective mass for electrons and holes, and the energy difference between the indirect gap and the direct gap is smaller. These electronic conditions lead to an expectation that it is much easier to change the electronic structure around the band gap of Ge. Therefore, Ge nanoclusters (nc) embedded in silica matrices have attracted intensive research interest during the past decade due to the unique electric and photonic properties, brought about by the quantum-confinement effect, and their potential applications in new generation nonlinear devices. Among these, optical memory [1, 2], light emitters [3-8] and enhanced third order optical nonlinearity [9-13] are the three main fields into which much effort has been put. At present, Ge nc have been successfully made by a lot of methods. These methods basically consist of two steps. The first step is...

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the fabrication of thin films, which provide the source of SiO₂ and Ge. The film fabrication methods have encompassed radio frequency (rf) or magnetron co-sputtering [3,5,6,9,11,13-16], ion implantation [10, 17-20], and plasma enhanced chemical vapour deposition (PECVD) [21,22] et al. After the deposition, the film is usually post-processed by annealing, electron beam irradiation or both.

In this paper, we present our recent progress on Ge nanoclusters made by both irradiation of electron beam and heat treatment of PECVD deposited thin films. For the first time to our best knowledge, we also demonstrated that the nanocylinders with Ge shell were formed by e-beam irradiation. The method of making Ge nanoclusters by heat-treating (or annealing) PECVD deposited thin films is completely compatible with the standard waveguide processing. Therefore, waveguide structures doped with these Ge nanoclusters have been fabricated and the preliminary optical characterization has been done.

2. GE NANOCLUSTERS AND GE SHELL NANOCYLINDERS FORMED BY E-BEAM IRRADIATION

2.1 Ge nanoclusters formed by e-beam irradiation

2.1.1 Experiments

Ge-doped glass thin films were deposited by PECVD using reaction gases: SiH₄, GeH₄, and N₂O. By varying the ratio between SiH₄ and GeH₄, the Ge concentration in the deposited film was adjusted. Two types of samples were prepared, sample A with a Ge concentration of 35 mol% and sample B with a Ge concentration of 50 mol%. The Ge concentration was measured by Rutherford backscattering spectroscopy (RBS). Usually the deposition time was set to 15 min, resulting in a film thickness of about 1.1 and 1.6 µm for type A sample and type B sample respectively. The Ge doped glass thin films were grown on a silicon substrate. After the deposition, the thin films were heat-treated at 1100 °C for 4 hours in N₂ for consolidation.

The prepared samples were examined by transmission electron microscopy (TEM) using a JEOL 3000F operated at 300 keV. Additional TEM experiments were carried out at 100 keV using a Philips EM430.

2.1.2 Results and discussion

![TEM cross-sectional image of sample A. Region 1 is the silicon substrate. Region 2 is Ge-doped glass. A semi-circular region in the Ge-doped area was caused by irradiation of focused electron beam. The beam diameter is about 450 nm.](image)

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A TEM image of sample A is shown in Fig. 1. It shows the interface between silicon substrate at the bottom (region 1) and Ge-doped glass at the top (region 2). In the micrograph, in which contrast is due solely to mass-thickness effects, the Ge-containing layer is easily distinguished from the silicon substrate because it is darker. Using these operating conditions, clusters of diameter greater than \(-2\) nm are resolvable. The semi-circle that is seen in the Ge-doped glass area formed due to irradiation by an electron beam with a beam diameter of 450 nm. The figure shows that there are nanoclusters, appearing as dark spots, in this area. The nanoclusters are seen to vary in diameter from approximately 4 nm at the edge of the irradiated region to 15 nm at the centre. Outside the well delineated area that has been irradiated by the electron beam, there are no visible clusters and the Ge is assumed to be in solid solution.

A high magnification TEM image of sample B with 50 mol% Ge concentration was taken after 5 minutes of electron beam irradiation, see Figure 2. By comparing to other TEM pictures taken with shorter irradiation time, we observed that the clusters under the focused beam both increased in size and eventually became crystalline. By comparing the TEM images taken with longer irradiation time, we observed that the size of clusters saturated at about 15 nm. The high resolution image showed lattice fringes of approximately 0.33 nm corresponding to the (111) crystal planes in germanium. It is noted that silicon or any Si/Ge alloy will have smaller lattice fringes.

![TEM image of sample A](image1)

![TEM image of sample B](image2)

**Fig. 2:** (a) TEM image of a cross-section of the interface. The silicon substrate is at the top of the image and the germanosilicate layer is at the bottom. The image was taken after 5 min. of electron beam irradiation. (b) High resolution TEM image showing the crystal planes of 3 clusters.

To investigate further how the electron beam affects the formation of clusters, similar electron beam irradiation was carried out using an electron beam energy of 100 keV and very similar results were obtained as at 300 keV. This preliminary set of experiments therefore indicates that the formation of Ge clusters is not dependent on the energy of electrons usually used for TEM observation.

To further understand the nanocluster formation, we changed the spot sizes of the electron beam during irradiation of sample A. In Fig. 3, the diameter of the electron beam is from left to right \(-70, 100, 140, 170, 200\) and \(-280\) nm, and denoted 1-6 respectively. The figure shows that when the beam is focused strongly, sites 1 to 3, the Ge seems to be pushed to the outer rim of the irradiated area, while the irradiated area itself appears very bright. As the beam is defocussed, well separated clusters start to appear in the gradually less bright appearing irradiated areas. At site 4, a single germanium nanocluster is observed. Then as several well separated clusters of varying size, sites 5 and 6. The elongation of site 1 is caused by specimen drift under the beam spot.
The brightness of the irradiated areas, in particular at the smallest beam diameters, site 1 and 2, can be explained as being due to two effects. One effect may be a decrease in mass contrast, as the Ge is transported from the centre of the irradiated area due to preferential Ge knock-on damage from electron collisions.

![TEM cross-sectional image of sample A. The specimen was irradiated at 6 sites with increasing beam diameters from left to right](image)

The observations presented in Fig. 3 suggest that the size of the clusters can be controlled by the electron beam irradiation dose. This is a very important observation since the size and distribution of the nanoclusters affect the optical property of the glass. Thus, by tuning the size and distribution, the optical properties of the material may be engineered.

Based on the results of TEM analysis, the Ge in PECVD deposited Ge-doped glass is suggested to be in solid solution in concentrations of up to 50 mol% in silica glass. During observation in the TEM, Ge clusters are seen to form due to electron beam irradiation. The Ge clusters first increase in size and then crystallize during prolonged electron beam irradiation. The formation of the clusters is sensitive to, and can be controlled by, variations in the electron beam intensity and irradiation time at an accelerating voltage of 300 kV.

### 2.2 Ge shell nanocylinders formed by e-beam irradiation

#### 2.2.1 Experiments

A Tecnai F20 Super Twin field-emission gun TEM (FEGTEM) operated in scanning mode at 200 kV was used to form nanocylinders and characterize the sample in three dimensions. The thickness of the irradiated area was 200 nm and the electron current was kept constant to 150 pA for a beam size of 0.4 nm.

The preparation of the samples is the same as in subsection 2.1.1.

#### 2.2.2 Results and discussion

Fig. 4 (a) shows a TEM image of an area irradiated with the e-beam in a scanning transmission electron microscope (STEM) from which a tomographic series in high angle annular dark field (HAADF) mode was acquired. The irradiation pattern consists of 4 rows of dots and several continuous lines. Each row contains 15 dots. For each row of dots, the dot was formed with different exposure times of 1, 2, 4 and 8 sec, respectively. Continuous lines were formed by reducing the distance between dots. Insets in Fig. 4(a) shows the diameter of the dots. They change with irradiation time. The diameters in the experiment were varied between 8 nm for 1 second and 16 nm for 8 seconds exposure. The widths of Ge walls does not change much with irradiation and it is about 5 nm. The compositions of the black dots and the surrounding bright area were analyzed by energy dispersive X-ray spectroscopy (EDS). Only element O, Si and Ge were detected. The density increase of Ge at the bright edge was observed.

Fig.4 (b) shows the corresponding 3D image extracted from a tomographic series. For the first time to our best knowledge, the 3D image in Fig.4(b) shows clearly that nano-cylinders are formed by e-beam irradiation. The combination of the tunability of the diameter of the cylinders and the accurate control of the position of the cylinders makes it a perfect method to make optical resonant cavities without considering the processing limits of standard lithography.
These preliminary results show that the size of germanium nanoclusters and nanocylinders may be controlled by the electron beam irradiation. This is a very important observation since the size and distribution of the nanostructures affect the optical properties of silica. Moreover, these results also indicate that different specimen thickness or different thickness of Ge doped silica could be used to produce everything in between dots and cylinders with different aspect ratios.

3. GE NANOCLUSTERS FORMED BY HEAT TREATMENT

As expected that single Ge nc or nanocylinder can be accurately made by e-beam irradiation. Therefore, this method is very suitable to make nanoscale components. In order to fabricate standard nonlinear planar waveguide components, Ge nanoclusters were created only with PECVD and annealing without electron beam irradiation, as described in this part. One big advantage of making Ge nanoclusters totally compatible with standard waveguide processing is that they can be easily applied in the waveguide structures. The fabricated waveguides were shown and characterized with respect to absorption.

3.1 Experiments

Multi-layer films were deposited by using PECVD (STS cluster system) with the alternation of Ge-doped glass layers and amorphous SiGe layers. The deposition started with a Ge-doped glass layer on top of a 4 inch, (001) oriented, 525μm thick silicon wafer. This deposition used 5 sccm SiH₄, 5 sccm GeH₄ and 1600 sccm N₂O as reaction gases, at a temperature of 300 °C, a process pressure of 400mTorr (~50Pa) and an applied rf power of 600W. Then, an amorphous Si/Ge layer was deposited by switching off the N₂O, while keeping the remaining parameters like 5sccm SiH₄, 5sccm GeH₄, pressure and power the same as glass deposition. The deposition time of the glass was varied. Usually, the SiGe layer deposition was set for 1 min, which led to a 0.15μm thick SiGe layer. For multilayer structures, the deposition

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started with a silica layer, and then followed by a SiGe layer. Then more layers were deposited in sequence as a alternating silica layer and SiGe layer.

After the deposition, the thin films were annealed at 1100 °C for 4 hours in a dry N₂ at ambient pressure.

The prepared samples were examined by transmission electron microscopy (TEM) using a JEOL JEM-3000F operated at 300kV.

The Raman spectra were measured at room temperature by using a DILOR XY spectrometer with a liquid nitrogen cooled CCD detector (140K) and a microscope entrance. All the spectra were excited with the 514.5nm line from an argon-ion laser. Calibration of the wavenumber scale was done to an accuracy of ±1 cm⁻¹ with liquid cyclohexane and neon gas lines superimposed on the spectra.

Secondary ion mass spectroscopy (SIMS) was measured by using ATOMIKA 4000 with O₂⁺ or Cs⁺ ion source. The beam energy ranged between 1keV and 15keV. A quadruple mass analyzer was used.

3.2 Results and discussion

3.2.1 TEM and HRTEM

Electron beam plays an important role during the formation of Ge nanoclusters from Ge-doped glass. Therefore, extreme caution has been taken here to reduce the effect of the electron beam when TEM pictures were recorded. An image of a 4-layer structure after annealing was shown in Fig.5(a). One 150nm thick layer with nanoclusters was clearly seen, marked as number 3 in Fig. 5(a). These clusters vary in size, and the maximum diameter of the clusters is 150nm, which is the thickness of this layer. These clusters appear as round and darker dots due to increased mass contrast. The Ge-doped glass layer is 500nm. Another 150nm thick porous layer is seen on the top surface. The formation of the porous surface layer is due to the evaporation of the Ge clusters during annealing at 1100°C. In comparison of layer 2, layer 3 is much whiter, which implies that a much lower Ge concentration in this layer.

A high resolution (HR) TEM image of one of the clusters is shown in Fig.5(b). Perfect lattice fringes of approximately 0.33nm, corresponding to (111) crystal planes in Ge, is visible.

Selected area diffraction (SAD) image from the clusters was shown in Fig. 5(c). A clear diffraction pattern exhibiting sharp spots is present, showing that the clusters are crystalline.

Composition of the different layers was analyzed by EDX during the TEM investigation. It was found out that the initial SiGe layer was turned into SiO₂ layer with Ge nanoclusters embedded after annealing. This is further confirmed by the later SIMS measurement.

![Fig.5(a)](image_url)

Fig.5 (a) TEM image of 4 layers structure: Si substrate is indicated as 1; 2 Ge-doped glass layers are indicated as 2; layer with Ge nanoclusters in is 3 and porous top layer is 4.

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3.2.2 Raman spectroscopy

Raman spectra of the same sample investigated by the above TEM were recorded from the top surface. Spectra of bulk silicon and germanium specimens were also recorded as reference. In Fig 6(a), 6 curves are shown. Curve Ge and Si are from mono-crystalline bulk reference materials. Curve D1, E1, E4 and E6 are from the same spot on the sample while changing the focus of the microscope from the top surface to deep inside the substrate. These 4 curves have 2 prominent peaks, one is located at ~300 cm\(^{-1}\), contributed from Ge, and the other is at ~520 cm\(^{-1}\), contributed from Si. Expanded views of these two peaks are shown in (b) and (c) for details. From Fig 2(b), we can see that the intensity of 300 cm\(^{-1}\) peak increases first, reaches a maximum, and then decreases as the focus is changed from the top surface to deep inside the substrate. The peak is strongest when the Ge nanocluster layer is in focus. The further the focus is away from the Ge nc layer, the weaker the peak becomes. Comparing with the monocristalline Ge peak at 302.1 cm\(^{-1}\), the peaks from Ge nc shift to 303.6 cm\(^{-1}\), 304.8 cm\(^{-1}\), 306.2 cm\(^{-1}\), 305.8 cm\(^{-1}\) corresponding to curves D1, E1, E4 and E6 respectively.
Moreover, the peaks from Ge nc are broader than that from mono-crystalline Ge. According to [16], a probable cause of the shift of Raman peaks is internal stress, with compressive stress exerted on the clusters causing the shift of the peak to longer wavelengths. Therefore, we infer that the Ge nc in our structure experience compressive stress and that the magnitude of the stress on these Ge nc at different depths in the layer may have different values. The broadening of the Raman peak is attributed to the size distributions in Ge nc.

Another point from Fig. 6(b) is that the Ge nc peak in curve E1 is even stronger than the monocrystalline bulk Ge. The reason could be the quantum effect or a porous top layer acting as a surface enhancement. Further investigations are being carried out to clarify this.

From Fig. 6 (c), the Si peak is seen to be insensitive to changes in the focus. For all the curves, this peak is located at 520.9 cm$^{-1}$, about the same as bulk Si, and the silicon peak is much weaker than the Ge peak. The position of the peaks overlaps with the monocrystalline bulky Si, which indicates that it comes from the Si substrate. The intensity ratio of the Ge peak to Si peak is almost the same for different focus. The absence of a signal at around 400 cm$^{-1}$, which would be related to Si-Ge bonds, further supports that the nanoclusters are composed of Ge exclusively.

Another conclusion that can be drawn from the weak Si peak is that Ge nc absorbed strongly at the wavelength of 514.5nm (Raman pump light) and 528.7 nm (Si Raman shift). Little pump light can pass Ge nc and reach Si substrate, and even much less Raman scattering light from Si substrate can go through Ge nc again and be collected by the detector.

![Graph showing Raman spectra from sample with Ge nc. Spectra from bulk Si and Ge are present as a reference. Spectrum D1, E1, E4, E6 and E8 are collected when changing the focus from the top surface of sample to deep inside the substrate.](image)

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3.2.3 SIMS

In order to analyze the composition change, especially in the Ge nanocluster layer, a trilayer structure (a glass layer ending as the top surface layer, acting as a cap to avoid evaporation of Ge during annealing) was prepared and SIMS measurements were made for both as-deposited samples and annealed samples for comparison. Three elements (O, Si and Ge) were analyzed through the 3 layers and the results are shown in Fig 7 (a) and (b), respectively. Three interfaces (SiO$_2$-Ge nc, Ge nc-SiO$_2$, SiO$_2$-Si) are clearly observed in both figures. Comparing (a) and (b), there is no visible difference for the Ge-doped glass layer. They have almost the same concentration with respect to elements O, Si and Ge. However, a big difference is seen in the middle SiGe layer. After annealing, O composition in the middle layer increases.
dramatically. Since the sample was annealed in N$_2$ at ambient pressure, the increase of O must come from the surrounding Ge-doped glass layer. The O source from glass layer could be some content of O rich non-stoichiometric SiO$_2$:Ge. The O could be released and diffused to the middle SiGe layer during the annealing, and turned the as deposited SiGe layer into a SiO$_2$ layer with Ge nc.

Fig. 7(a) SIMS depth profile of the as-deposited trilayer structure on top of Si substrate. Solid black line, dotted blue line and dashed red line are secondary ion intensity of Si, Ge and O respectively.

Fig. 7(b) SIMS depth profile of the trilayer structure after annealing at 1100 °C for 4 hours. Solid black line, dotted blue line and dashed red line are the secondary ion intensity of Si, O and Ge respectively.
3.2.4 Multi-Ge nanocluster-layer structure

Multi-Ge nc-layer structures can be readily achieved by using the same PECVD deposition and annealing. A scanning electron microscope (SEM) image of a 7-layer structure is shown in Fig. 8, where 3 Ge nc layers were sandwiched by 4 glass layers. Since one of the potential applications of this structure is the fabrication of nonlinear waveguide components, this method can be easily adopted for mass-production.

![SEM cross-sectional image of a 7-layer structure: 3 Ge nc stripes (marked as 1) plus 4 glass layers (marked as 2)](image)

4. FABRICATION AND CHARACTERIZATION OF GE NANOCLUSTERS DOPED WAVEGUIDE

4.1 Experiments

The fabrication of Ge nanoclusters doped waveguides starts with 4 inch silicon wafers. The processing steps consist of growth of buffer layer, deposition of core layer, etching of core layer, and deposition of top-cladding layer. They are same as that of standard waveguide fabrication [23], except that all the annealing is in N\textsubscript{2} atmosphere instead of wet O\textsubscript{2}, to avoid the oxidation of Ge nanoclusters.

The optical characterization of Ge nanoclusters doped waveguides used a broadband source, super K, with wavelength ranging from 500nm to 1700nm. A polarizer and a polarization controller were connected between the light source and the measured waveguides. Optical spectral analyzer (OSA) was used to detect the signal from the output of the waveguides.

4.2 Results

Buried waveguides with one strip or multiple strips of Ge nanoclusters have been successfully made. A SEM cross-sectional view of one buried waveguide with one strip of Ge nanoclusters embedded in the core is shown in Fig. 9(a). The core of the waveguide is rectangular, buried in the surrounding top-cladding glass. A strip of Ge nanoclusters is at the middle depth of the core. The size of the core is about 3.5x3.5 μm\textsuperscript{2}. Fig. 9(b) is the zoom in of part of the core area, which shows clearly the Ge nanoclusters.
This type of waveguides have been characterized with respect to absorption. The transmission spectra of a standard waveguide and a Ge nanoclusters doped waveguide together with super K light source are shown in Fig. 10 from wavelength of 500nm to 1700nm. We can see from the figure that the loss of a standard waveguide is a constant about 5 dB for the whole wavelength range. However, Ge nanoclusters doped waveguide have a much larger loss, around 25dB. Two prominent absorption peaks show up for the Ge nanoclusters doped waveguide. One is at around 1400nm and the other one is at around 1100nm. For the wavelength shorter than 900nm, the Ge nanoclusters doped waveguide is opaque.

Doping the Ge nanoclusters in the structure of a waveguide means all the know-how to characterize an optical waveguide can now be applied to Ge nanoclusters. This will speed up knowing the properties of these Ge nanoclusters.
5. CONCLUSION

By combining standard waveguide deposition technique, we have successfully created Ge nanostructures (including Ge nanoclusters, and nanocylinder with Ge shell) from PECVD deposited films by two methods. One method is using high energy e-beam irradiation of Ge-doped silica. Ge nanoclusters appear, grow big, and become crystalline with the prolonged irradiation time. The size and distribution of the Ge clusters are very sensitive to the focus of e-beam. For the first time, nanocylinders with Ge shells are demonstrated after the irradiation of a very focused e-beam. This method is very suitable to make nano-scale devices. The second method to make Ge nanoclusters is heat-treatment. Bigger Ge nanoclusters are formed in an as-deposited SiGe layer sandwiched by glass layers. The as-deposited SiGe layer was turned into Ge nanoclusters doped silica layer after the heat treatment in N₂. This method is more suitable to make standard waveguide components in a micrometer scale. Buried waveguides doped with Ge nanoclusters have been made and the preliminary characterizations have been done. Further investigation of the physics behind these results are ongoing.

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