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Structural, mechanical and optical properties of Ge nanocrystals embedded in superlattices fabricated by *in situ* low temperature annealing

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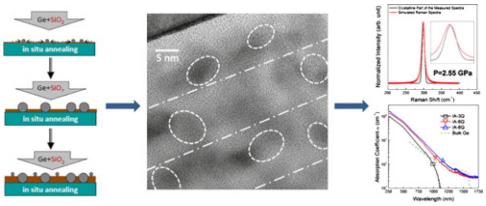
HIGHLIGHTS

- ► Ge nanocrystals were grown in superlattices by *in situ* annealing.
- ► A core–shell structure was observed as due to the lower annealing temperature.
- ► The *in situ* annealing process produced significant compressive stress.
- ► Optical properties of superlattices were influenced by Ge nanocrystals.
- ► Quantum confinement was observed in the optical properties of superlattices.

GRAPHICAL ABSTRACT

Size controlled Ge nanocrystals were fabricated by *in situ* low temperature annealing and their structural, mechanical and optical properties were investigated in detail.



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ABSTRACT

Ge nanocrystals (Ge-ncs) embedded in SiO_2 superlattices were prepared by *in situ* low temperature annealing. The formation of size controlled nanocrystals was demonstrated by Raman scattering, X-ray diffraction and transmission electron microscopy measurements. A core–shell structure was observed in the *in situ* grown Ge-ncs as a result of the lower annealing temperatures. The *in situ* annealing process also produced significant compressive stress in the superlattices, and the calculation result shows that the hydrostatic pressure induced by the compressive stress was about 2.55 GPa for the nanocrystals with average size of 7.1 nm. The optical absorption edges of the *in situ* grown superlattices moved to lower wavelength as crystallite size decreased. The presence of Ge-ncs enhanced the film absorption at short wavelength and the absorption coefficient was found to increase in superlattices containing larger nanocrystals. The superlattices exhibited optical band gap energies larger than that of bulk Ge and a blueshift of energies was observed with the decrease of crystallite size. These features are tentatively explained by quantum confinement effect in the Ge-ncs. Our results indicate that *in situ* low temperature grown Ge-ncs and superlattices are promising candidates for the fabrication of nanoscale devices on low cost substrates.

1. Introduction

Group IV nanocrystals have attracted increasing interest during the past few decades [1–7]. In contrast to Si nanocrystals (Si-ncs), much less work has been done on the exploration of other candidates, such as Ge nanocrystals (Ge-ncs). In fact, Ge-ncs have their own advantages under certain circumstances. Particularly, the lower process temperature of Ge-ncs is of special interest for thin film applications, since it enables the capability of device fabrication on low cost or flexible substrates.

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The exclusion of high temperature parts also helps to reduce the manufacturing complexity. These are indeed great advantages for both processing compatibility and long term processing cost.

In conventional approaches, Ge-ncs embedded in SiO_2 matrix are prepared by thermal annealing at temperatures of about 700 °C or above [6–10]. So far, many efforts have been made to understand the properties of Ge-ncs fabricated through these methods. Although this range of temperature is already much lower than that required for the growth of Si-ncs (typically around 1100 °C), it is still too high for glass or polymer substrate based processes. Therefore, further reduction of growth temperature is quite important for improving the competitiveness of Ge-ncs.

Recently, our group has developed a low temperature technique for the preparation of Ge-ncs embedded in SiO_2 matrix [11]. Instead of post-deposition annealing, *in situ* substrate heating is used during the thin film deposition, and the growth temperature of Ge-ncs is considerably reduced to lower than 400 °C. Comparing with the few other low temperature approaches [12–16], this technique is simple and allows for the silicon process integration. Hence it is very promising for the fabrication of low cost quantum devices based on Ge-ncs. Nevertheless, a thorough understanding of the properties of the low temperature grown Ge-ncs is required prior to the realization of functional devices.

In this paper, Ge-ncs embedded in SiO_2 superlattices were prepared by *in situ* substrate heating and their properties were systematically investigated. The structural features of Ge-ncs were characterized by transmission electron microscopy (TEM), glancing incidence X-ray diffraction (GIXRD) and Raman scattering measurements. A simple method based on the phonon confinement model was used to determine the residual stress and hydrostatic pressure presented in the superlattices. The dependence of residual stress on growth substrate and annealing methods was also discussed. The optical absorption properties of the *in situ* grown superlattices were measured by UV–visible–NIR spectrophotometer and the optical band gaps of Ge-ncs with different crystallite sizes were extracted from the absorption spectra.

2. Experimental details

Ge-ncs embedded in superlattices were fabricated by magnetron sputtering and *in situ* annealing. Samples were grown both on silicon and quartz substrates to facilitate structural and optical characterization. The sputtering target was a 4 in. circular fused silica plate uniformly partially covered with six pieces of fan-shaped Ge strips (99.9999% purity). The growth chamber was pumped down to a base pressure of 3.0×10^{-4} Pa and the thin films were deposited at 25 W power. Alternative layers of Ge-rich SiO_2 (GeRSiO) and a mixture of stoichiometric oxides (GeO_2/SiO_2) were deposited by Ar sputtering at a pressure of 0.1 Pa and by reactive sputtering with oxygen at a pressure of 0.2 Pa, respectively. The deposition started with the GeO_2/SiO_2 layer as a barrier to block impurity diffusion from the substrate. GeRSiO layers with different thicknesses were grown by varying the sputtering time while the thickness of GeO_2/SiO_2 spacing layers was kept constant with a sputtering time of 6 min. The number of bi-layers differed depending on the sputtering time in order to ensure that the accumulative thickness of GeRSiO layers was comparable in all samples. At last, a GeO_2/SiO_2 capping layer was grown to prevent possible penetration of moisture and oxidation of Ge-ncs during storage and measurement. During sputtering process the substrate was intentionally heated up to ~360 °C for *in situ* growth of nanocrystals, and the samples with same deposition time for individual GeRSiO layer were grown together in a single process batch. Besides low temperature grown samples, Ge-ncs were also prepared by post-deposition high temperature annealing at ~700 °C for comparison purpose. Details of the superlattices, such as sample ID, growth substrate, sputtering time for individual GeRSiO layer, and number of periods are given in Table 1.

Table 1
Details of the structural parameters of the prepared superlattices.

Growth method	**Sample ID**	**Growth substrate**	**Sputtering Time for individual GeRSiO layer** (min)	**No. of periods**
In situ annealing	IA-3S	Silicon	3	10
	IA-3Q	Quartz	3	10
	IA-6S	Silicon	6	7
	IA-6Q	Quartz	6	7
	IA-8S	Silicon	8	5
	IA-8Q	Quartz	8	5
Post-annealing	PA-6S	Silicon	6	7
	PA-8S	Silicon	8	5

3. Results and discussion

3.1. Structural properties

In order to detect the presence of Ge-ncs in superlattices, Raman scattering spectra were measured by Renishaw's RM200 micro-Raman spectrometer. The beam was excited by an Argon laser with a wavelength of 514.6 nm and a spectral resolution of 1–2 cm^{-1}. A laser power lower than 2.5 W was used in order to rule out the spurious post-annealing effect induced by the laser heating. Fig. 1 shows the Raman spectra for *in situ* grown superlattices deposited on both silicon and quartz substrates. Also included in the figure are the spectra for non-annealed superlattice and bulk crystalline Ge. The sharp peaks of the samples are centered very close to the Ge-Ge optical phonon mode for bulk Ge at 300.4 cm^{-1}, which confirms the formation of crystalline Ge-ncs in the thin films. All spectra in the figure exhibit broadening at lower frequencies due to the confinement of phonons in small crystallites [17–19]. The folding of optical phonons allows phonons of lower energy to occur at zone center and hence be optically active; in other words, the requirement for full momentum conservation during Raman scattering is relaxed in these nanoparticles. It is also noticed that superlattices with thicker individual GeRSiO layer such as IA-8S and IA-8Q exhibit more symmetrical Raman peaks. As a superlattice, it has the ability to limit nanocrystal size via the GeRSiO layer [11], so the greater broadening in superlattices with thinner GeRSiO layer may be because of the smaller crystallite size which induces greater phonon confinement. Meanwhile, Ge-ncs are likely to have a core–shell structure with an amorphous interfacial layer separating crystalline core and surrounding matrix [20–22]. Therefore, the larger surface to volume ratio in smaller nanocrystals could result in a larger total volume of amorphous components which contributes to the greater hump at lower frequencies. Comparing Fig. 1(a) with (b), we notice that the Raman peaks for thin films grown on quartz substrates are not as sharp as those on silicon substrates, which is probably attributed to the different growth conditions. Although samples of the same deposition time for individual GeRSiO layer were processed together, the thermal response of silicon and quartz substrates to the carbon heater is different. The lower thermal conductivity of quartz substrates may have lead to lower substrate temperature which results in poor crystallinity of Ge-ncs.

Crystalline properties of *in situ* grown Ge-ncs were further studied by GIXRD using Philips's X'Pert Pro materials research diffraction system. The diffractive patterns of the superlattices deposited on quartz substrates are shown in Fig. 2. All three