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Role of rapid thermal annealing in the formation of crystalline SiGe nanoparticles

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ABSTRACT

In the present work, we report the formation of SiGe nanoparticles embedded in SiO_2 film by atom beam sputtering method in conjunction with Rapid Thermal Annealing (RTA). Crystalline SiGe nanoparticles in the co-sputtered films are formed after rapid thermal annealing at 900 °C and 1000 °C for 1 min in N_2 gas ambient. These nanoparticles were characterized using UV–vis absorption, GXRD, FTIR and Raman measurements. UV–vis spectra show blue shift of absorption edge with the increase in annealing temperature. GXRD pattern shows that particles formed are crystalline. The average size of the nanoparticle estimated from GXRD is 15 nm to 30 nm for the films annealed at temperatures 800 °C and 1000 °C respectively. FTIR spectra show the phase separation between SiGe nanoparticles and SiO_2 matrix after RTA. Raman spectra show that SiGe phase is formed with c-Ge as core and c-SiGe as shell in the SiO_2 matrix.

1. Introduction

$Si_{1-x}Ge_x$ alloys have attracted much interest since the early 1970s due to their band gaps being variable between those of bulk Si and Ge via a so called "band-structure engineering" [1] and their compatibility with the Si technology [2]. Band gap tuning is possible by varying the concentration of Si and Ge. SiGe is a good candidate for monolithic integrated devices for the optical communication wavelengths [3]. Kolobov et al. [2] synthesized GeSi nanocrystals in SiO_2 matrix by co-sputtering of Ge, Si and SiO_2 targets on to a silicon substrate and RTA annealing at 800–1000 °C for 300 s in N_2 ambient. An isotropic and relaxed c-Ge core is formed after annealing at or above 900 °C followed by the formation of a-GeSi phase [2]. RTA has advantages over conventional furnace annealing (CFA) that it leads to lower crystallization temperature, very short annealing times (second for RTA vs hours for CFA), significantly reduced thermal budget, minimized film substrate interface reactions and better electrical properties [4]. An increase in heating rate reduces both the annealing temperature and time required for transformation.

In the present work, we explore the possibility of forming SiGe nanoparticles using atom beam co-sputtering and subsequent rapid thermal annealing of the Ge, Si, SiO_2 composite films. The films were characterized using UV–visible spectra, GXRD, Raman, and FTIR measurements.

2. Experiments

In atom beam sputtering [5], a fast Ar atom source is installed in a vacuum chamber pumped by a turbo pump. The atom source is mounted at an angle of 45° facing towards the sputtering target. The source delivers a maximum current density of 30 μA/cm^2 on the target and with energy about 1.5 keV. The area of the beam was approximately 50 mm diameter. The sputtering target consisted of a circular SiO_2 plate (diameter ~7.65 cm) on which Ge (area ~1150 mm^2) and Si (area ~1150 mm^2) pieces were distributed uniformly so that the area ratio of SiO_2:Si:Ge was 2:1:1. The substrate holder was mounted on a DC motor and rotated to obtain uniform deposition. The target to source distance was 10 cm. The deposition was carried out for 8 h. The films were deposited on fused silica (1 cm × 1 cm × 0.15 cm) and Si wafer (100) of resistivity of 8–12 Ω-cm. Pressure in the sputtering chamber was 10^{-6} mbar (10^{-4} Pa) which was increased to create Ar plasma to a pressure of 1.5×10^{-3} mbar (0.15 Pa). Samples were annealed in a RTA furnace [6] in N_2 ambient for 1 min at different temperatures from 800 °C to 1000 °C.

The as-deposited and annealed films were characterized using UV–visible-NIR spectrophotometer of Shimadzu model UV-3600 in transmission mode. Glancing angle X-ray Diffraction (GXRD)

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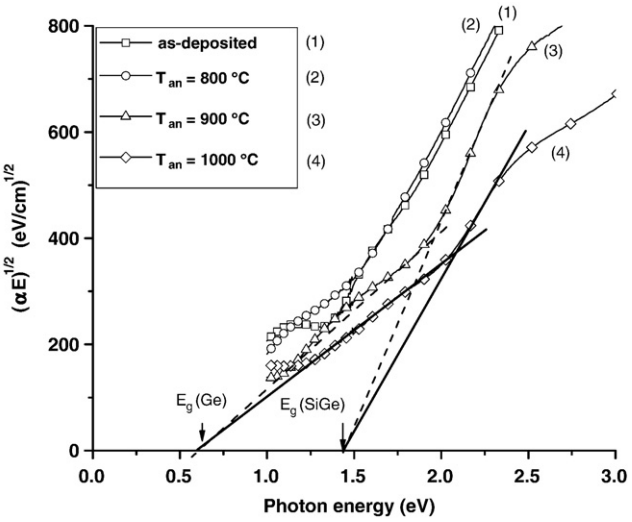

Fig. 1. Plot of $(\alpha E)^{1/2}$ vs E obtained from UV–vis spectra for as-deposited and samples annealed at $T_{an}=800$, 900, 1000 °C as shown by curves (1), (2), (3) and (4). Extrapolated lines for curve (3) (– –: dash) and curve (4) (—: solid) give intercept on energy axis as band gaps.

measurements were carried out using X'pert-PanAnalytical XRD machine. X-ray source produces Cu–K_α line with wavelength of 1.54 Å scan range = 20–60°, step = 0.025, time = 2 s and angle of incidence = 1°. Instrumental broadening was 0.05°. Raman spectra were recorded in backscattered geometry on Jobin–Yvon instrument with Ar ion laser (λ = 514 nm). FTIR spectra were measured having a scanning range from 400–4000 cm^{-1} by using JASCO model-610. Rutherford Backscattering Spectrometry measurements were carried out to estimate the film thickness and the concentrations Si, Ge and O in the films.

3. Results and discussion

RBS analysis of the as-deposited film shows that the Si:Ge:O contents in at.% are 24%:42%:33% respectively. Since the sputtering rate of Ge is almost double the sputtering rate of Si and SiO_2, the Ge content is larger than that of Si. The thickness of the films estimated from the RBS analysis is 255 nm. Fig. 1 shows the Tauc plot [7] obtained from the UV–visible-NIR spectra of the samples formed by atom beam sputtering and subsequently rapid thermal annealed at

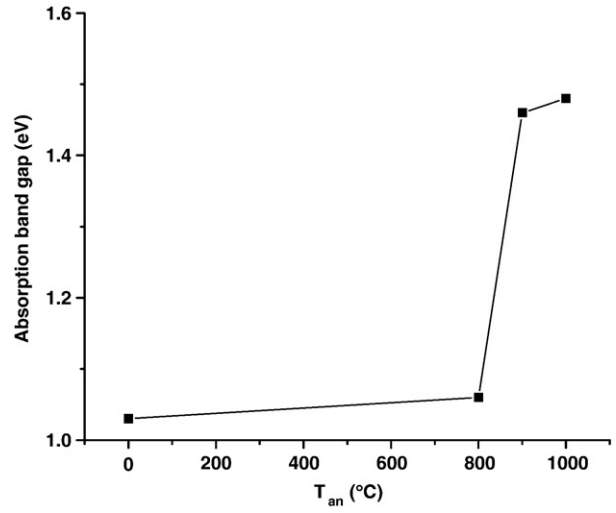

Fig. 2. Plot of absorption band gap variation for SiGe nanoparticles with annealing temperature (T_{an}).

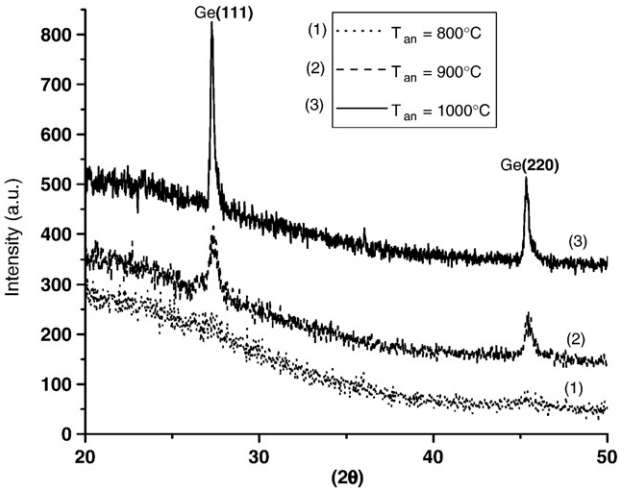

Fig. 3. GXRD plots of samples RTA annealed at 800, 900 and 1000 °C for 1 min in N_2 atmosphere as shown by curves (1), (2) and (3) respectively.

800, 900, 1000 °C for 1 min in N_2 atmosphere. Curves (3) and (4) clearly show two slopes which when extrapolated to x-axis indicate that two materials having two different band gaps are present in the samples. The band gap can be estimated from the Tauc plots using the following relation,

$$(\alpha E)^{1/2} = B\left(E - E_g\right)$$

Where, α is the absorption coefficient in (cm^{-1}), E is the photon energy, E_g is the bulk band gap of Ge as our particles are Ge rich. Thus the absorption edges for curves (3) and (4) are 0.62 eV and 0.6 eV for annealing temperatures of 900 °C and 1000 °C, respectively and which indicates the similarity in the formation of nc-Ge. Absorption edges due to nc-SiGe are 1.03, 1.06, 1.46, 1.48 eV for as-deposited and samples annealed at $T_{an}=800$ °C, 900 °C, 1000 °C respectively. The absorption edge gets blue shifted with the increase in annealing temperature as shown by curves (2) to (4) for the edges corresponding to nc-SiGe. Fig. 2 shows the variation of the absorption band gap of SiGe obtained from the Tauc plot with annealing temperatures.

Fig. 3 shows the GXRD spectra of RTA annealed samples deposited on silicon substrates. Crystallization of the films took place rapidly in a short duration of time (1 min) due to RTA. GXRD pattern shows that films are polycrystalline. Assuming that the contribution due to the strain is negligible, the composition of the nanoparticles was estimated using Vegard's rule which in our case is given by ($a = 5.431 + 0.227x$) [8,9]. Curve (3) shows that there are 2 main sharp peaks and a shoulder which could be due to SiGe nanoparticles or stresses present in the sample. XRD peaks in curve (3) at $2\theta = 27.29°$ and 45.37° are due to c-Ge (from JCPDS data-file no.04-0545) and correspond to (220) and (111) planes, respectively. Size of the nanoparticles (D) was estimated from the Scherrer formula given as $D = 0.89\lambda/[\beta(2\theta_B)\,\mathrm{Cos}(\theta_B)]$ [10]. Where, λ is the X-ray wavelength

Table 1
List of peak positions (2θ), (hkl), d spacing, lattice constant (a) and Ge content (x) variation with annealing temperature (T_{an}).

T_{an} (°C)	Peak position (2θ)	(hkl)	d spacing (A)	FWHM (°)	Lattice constant a (A)	x Ge content
800	45.2	220	1.08	0.68	5.656	0.99
900	27.3	111	3.26	0.54	5.65	
	45.5	220	1.99	0.58	5.63	0.88
1000	27.3	111	3.26	0.22	5.65	
	45.4	220	1.99	0.28	5.63	0.88