Photoluminescence study of $Si_{1-x}Ge_x$ nanoparticles in various oxide matrices

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Abstract— We investigate the photoluminescence properties of structures comprising of $Si_{1-x}Ge_x$ nanoparticles (NPs) within SiO_2, GeO_2, TiO_2 and Ta_2O_5 oxide matrices. Of the investigated structures, it was observed that the structures with GeO_2 and TiO_2 matrices provide increased spectral response (at ~907 and 844 nm respectively) and increased PL intensity. The improved PL characteristic have been attributed to increased diffusion barrier against oxygen which otherwise would result in formation of unwanted oxide at the film-oxide interface, thereby deteriorating the optical properties.

Keywords- SiGe, nanoparticles, photoluminescence, oxide

1. Introduction

Self-assembled quantum dots/nanoparticle (NPs) embedded in a dielectric oxide matrix exhibiting strong quantum confinement, have gained continual interest due to their application in optoelectronics and nanosized structures working in the visible to infrared region [1]. Various oxide matrices have been suggested in this regard including SiO_2, TiO_2, Al_2O_3 and HfO_2 [1,2]. In such system the interface betwen embedded NPs and the oxide, the diffusivity of Si, Ge and O, and the type of strain exerted by the matrix has been a matter of concern [1,3,4], all of which can result in alteration of the NPs bandgap energy.

The present work deals with influence of various oxide matrices on the photoluminescence (PL) characteristics of embedded SiGe NPs. It was observed that SiO_2 remains amorphous upto anneal temperature (T) of 800 ºC while GeO_2, TiO_2 and Ta_2O_5 were crystalline. An increased PL intensity and spectral resposne has been observed for NPs in GeO_2 and TiO_2 structures.

2. Experimental

A multilayered structure (ML) with stacking order of oxide/SiGe/oxide was prepared by magnetron sputtering over a 10×10 mm^2 SiO_2/Si(001) substrate. For the $Si_{1-x}Ge_x$ films (~20 nm), co-sputtering was carried out via direct current magnetron sputtering (dcMS) in constant power mode at 0.7 Pa, from individual targets of (6N purity) Si (80 W) and Ge (15 W), respectively. The deposition rates were adjusted to obtain Si/Ge ratio of 75/25.

Various oxide matrices having a constant thickness of ~40 nm was utilized in this study (i.e., SiO_2, GeO_x, TiO_2, and Ta_2O_5, and will be denoted as ML_1, ML_2, ML_3 and ML_4, respectively). For the oxide layers, deposition was carried out via reactive-dcMS sputtering. The argon (Ar) (q_{Ar}= 40sccm) and O_2 flow rates were adjusted via mass flow controller. After deposition, the structure underwent annealing for 1 min in a rapid thermal processor (RTA, Jipelec JetFirst 150), in N_2 ambient. The structural investigation of the fabricated MLs was carried out by grazing incidence X-ray diffraction (GIXRD) [3]. A detailed description of the PL measurements and its setup can be found elsewhere [5].

3. Results and Discussion

Fig. 1, shows the GIXRD scans of structures (M_1-M_4) annealed at 800 ºC for 1min. For each structure, an evident presence of a SiGe peak positioned between standard Si and Ge peak position [3] was observed. For SiO_2 the GiXRD shows an amorphous matrix, whereas for GeO_2, TiO_2 (anatase) and Ta_2O_5, peaks implying crystalline nature of oxide

matrix can be observed in **Fig 1**. The average NP size obtained using XRD scans were found to be ~11, 33, 29 and 16 nm, for M_1 to M_4, respectively. The structure comprising of SiO_2 and TiO_2 matrices have already been studied in our previous works [3,4]. The average NP size determined there was in good agreement to that observed via TEM analysis. Moreover, for ML_1 and ML_4, one can observe a SiGe peak closer to the standard Si position while in the case of GeO_2 matrix i.e., ML_2 the peak is closer to the Ge standard position. Such an effect of the oxide matrix is due to increased diffusion barrier in case of ML_2 and will be elaborated further. In case of ML_4 the SiGe peak position overlaps with the Ta_2O_5 (1 11 0) peak position.

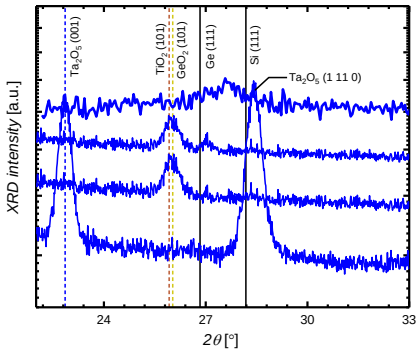

Fig. 1. XRD scans for structure having varying oxide matrices. The solid line shows the standard (111) peak positions for Si and Ge, while the colored dotted line shows crystalline peaks for standard GeO_2, anatase-TiO_2 (red) and Ta_2O_5(blue).

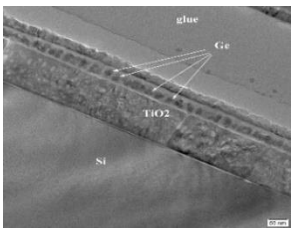

Fig. 2. TEM image for structures comprised of SiGe betweenTiO_2 matrix annealed at 600 ºC. resulted in formation of unwanted oxide at the film-oxide interfaces [3].

A common downside of annealing such structures, is the formation of unwanted oxide (for instance in **Fig. 2**) at the interface between SiGe and the oxide [1,3,6], possibly due to phase separation of SiGe at elavated temperature and inter-diffusion of oxygen from the oxide matrix. Since formation of SiO_2 is more exothermic than that of GeO_2, and that Ge has lower diffusion coefficient than Si, annealing at elevated temperatures will result in Ge seggregation and formation of unwanted oxide layer [7]. Such formation of additional oxide layer at the interface tends to deteriaorate the interface morphology and the optical properties [8]. However, such issues have been overcome in our previous studies having similar structures [1,3,4,9].

The photoluminescence obtained from SiGe NPs in oxides are dominated by; defect-related emission in the UV-regime, band-to-band transition, localized states within the oxide (i.e., oxygen vacancies), NPs posing quantum confinement effect and the interface between the NPs and the oxide matrix [5,10]. However in this current study the origin of the observed PL peaks is not discussed.

Fig. 3(a, b) shows room temperature (RT) PL spectra of structures having varying oxide matrices annealed at temperature (*T*) of 550 and 800 ºC, for 1 min. A clear variation in PL intensity was observed which was found to be highest for ML_2 and ML_3 and lowest for ML_4. However, for all the structures annealed at low *T*, broad PL spectra was observed with peak maxima at ~ 596, 640, 582 and 514 nm for structures M_1-M_4, respectively. With an increase in anneal *T*, ML_1 and ML_2 structures showed a broad hump with small peaks at lower λ and a relatively high intensity peak at λ = 840 and 907 nm. For ML_3 and ML_4, a significantly high intensity peak at λ ~ 844 and 842 nm was observed with suppressed signals at lower λ. Of the mentioned structures (annealed at *T* of 800 ºC), ML_2 showed the extended response with peak maxima at 907 nm and will later be discussed further.

The broad peak observed for M_1-M_4 structures (annealed at low *T*) and for ML_1-ML_2 (annealed at high *T*), can be attributed to wide size distribution of NPs [11,12] and the strain exerted by the oxide matrix which in turn determines the size and shape of the NPs. In most cases, the difference in thermal expansion coefficient between NPs and the oxide matrix and the degree of matrix ordering are held responsible [13]. That is, annealing of the structure results in ordering of the oxide

matrix which governs the accommodation of growing NPs and strain exerted on them, thus altering the bandgap energy. Additionally, the effect due to lattice mismatch between the film and the oxide and Si-Ge cannot be neglected [4]. Furthermore, it has been documented in earlier studies [4,10] that for amorphous oxide matrix (i.e., ML_1), strain energy is minimized due to lower lattice mismatch and consequently, the NPs assumes spherical shape having the lowest interface energy. On the contrary, the strain energy increases in case of crystalline matrix. Hence the NPs prefer elongated shape to reduce the overall energy of the system by reducing the contribution of strain exerted by the matrix.

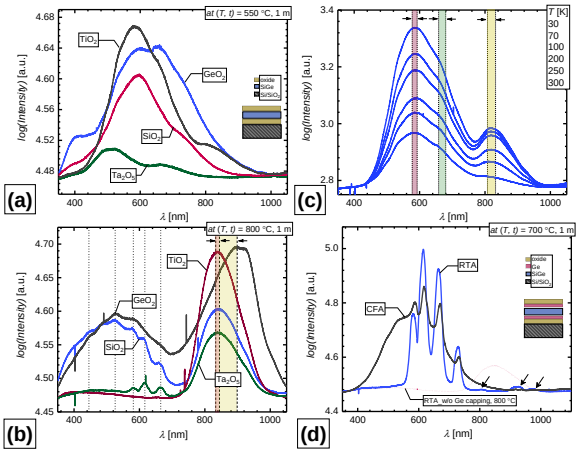

Fig. 3. Room temperature PL spectra of structure having varying oxide matrix (indicated in the figure) annealed at (a) 500 ºC and (b) 800 ºC for 1 min. (c) PL spectra measured at 300 K down to 30 K, for ML_3 structure annealed at 550 ºC. (d) PL spectra of TiO_2/Ge/SiGe/Ge/TiO_2 annealed at 700 ºC in RTA (1 min) and furnace annealing (CFA, 30 min).

Besides the effect from oxide ordering, the alteration in dielectric constant (highest for Ta_2O_5) of the surrounding oxide material plays a vital role in determining the exciton energy, thereby governing the PL intensity and relative change in peak position [14]. That is, the exciton energy increases as the dielectric constant increases [8]. Moreover, the defects related to non-stoichiometry in the oxide can alter the bandgap energy, which is usually higher for amorphous oxides than for crystalline matrices. That is, for amorphous matrix a higher number of oxygen vacancies results in increased number of dangling bonds which acts as recombination center creating energy states near the conduction band edge of oxide. For GeO_2 oxide, the increased PL intensity can be attributed to the fact that at elevated temperatures Si diffusing from the substrate into the GeO_2 will reduce GeO_x into Ge [6], thereby resulting in Ge rich NPs (as evident by GiXRD showing peak closer to bulk Ge). Furthermore, since the Ge has lower diffusion coefficient and enthalpy of oxygen than Si. The transfer of oxygen in the ML_2 structure predominantly creates SiO_2 at the matrix-substrate interface instead of volatile GeO and SiO [15]. Moreover, the migration energy of oxygen vacancy is much lower in GeO_2 than in SiO_2 i.e., facilitating formation of Ge-Ge and/or Si-Si bonds. Therefore, a dominant peak is observed at higher λ because of Ge rich NPs, and increased PL intensity due to reduction in oxide formation at interface.

For anatase-TiO_2 and Ta_2O_5 crystalline matrices, the variation in PL intensity can be explained on basis of the dielectric constant, thermal expansion (lower for anatase-TiO_2), and its lattice mismatch with the film (i.e. in-plane *a*-lattice is much higher for Ta_2O_s, than for anatase-TiO_2, thus altering the strain nature and size of NPs), which can greatly affect the lattice vibration and give rise to surface polarization effects (thereby altering the band structure and the PL intensity) [4]. Additionally, TiO_2 tends to increase diffusion barrier for Ge compared to Ta_2O_5, where the XRD-peak is closer to standard Si position. It is noteworthy to mention here that having rutile-TiO_2 can further enhance the PL-characteristic as has been discussed in earlier studies [5].

To scrutinize the PL peaks associated with NPs the ML_3 structure annealed at 550 ºC was analyzed via low temperature PL analysis (**Fig. 3c**). The spectra showed a shift in peak positions indicated by highlighted regions due to bandgap temperature dependence of NPs [12].

Fig. 3d shows a structures having thin Ge buffer layer between film and oxide matrix annealed at 700 ºC. It was observed that incorporation of thin Ge layer tends to increase the PL intensity (~an order

magnitude higher) with more defined spectral peak feature, than that of ML_3 [1,3]. Such an efect can be attributed to reduction in diffusion of oxygen and Ge into the film as the Ge tends to acts a a sacrifical layer and that the SiGe NPs obstained in this case is rich in Ge compared to ML_3, thus one case observe small peaks at higher λ (at ~926 and 977 nm) indicated by arrows. A comparison of RTA (1 min) vs. CFA (30 min) has been made, showing relatively well-defined PL-peaks for RTA processed structure, as a consequence of size controlled NPs and reduction in diffusivity of oxygen into the active film and/or Ge out-diffusion [6,16].

4. Conclusion

In summary, $Si_{1-x}Ge_x$ NPs embedded in varying matrices were fabricated and analyzed for their PL properties. It was observed that the surrounding oxide matrix can alter the PL characteristics. Of the studied structures NPs within GeO_2 and TiO_2 oxide provide increased PL intensity with peak maxima at ~907 and 844 nm. Which for GeO_2 is assigned to increased diffusion barrier characteristics to oxygen in to the SiGe film compared to SiO_2, while in case of TiO_2 it is assigned to the highly crystalline nature of the oxide giving better control over the NPs size distribution and stoichiometry. However, a better understanding on the diffusion barrier and strain imposed by Ta_2O_5 and TiO_2 (anatase and rutile polymorphs) is under investigation.

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