Defect free visible photoluminescence from laser-generated germanium nanoparticles

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Abstract

Origin of room temperature visible photoluminescence (PL) from defect free germanium (Ge) nanoparticles have been discussed here. The Ge nanoparticles produced by laser-induced etching technique show broad visible PL around 2.0 - 2.2 eV at room temperature. Size dependent PL peak shift in Ge nanoparticles has been explained in terms of quantum confinement. Theoretical calculations of radiative lifetime using oscillator strength, which is closely related to the size of the nanostructures, suggests that the PL is originating from a radiative recombination process in quantum confined Ge nanostructures.

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1 Introduction

Visible electroluminescence and photoluminescence (PL) from germanium (Ge) nanoparticles have received considerable attention in the last few years due to its potential applications in multifunctional electronic and photonic devices [1-4]. The luminescent Ge nanoparticles can be fabricated by several methods such as rf-magnetron cosputtering, ion-implantation, dc-sputtering in a reactive oxygen environment, chemical vapor deposition technique or by oxidation of Si-Ge alloys with subsequent thermal annealing to induce the crystallization [2-9]. In most of the reports, Ge nanoparticles are embedded in a SiO2 matrix and the observed PL spectrum is broad band around 2.0-2.4 eV [5, 8]. PL band near 1.83 eV is also reported by some researchers [5]. It is reported that Ge nanoparticles excited by 488.0 nm emits a visible PL around 2.2 - 2.3 eV which is independent of size in the 6 - 14 nm range [4]. However, Y. Maeda and coworkers [2] attributes the visible PL in the range of 2.0 - 2.3 eV to quantum confinement effect in Ge nanoparticles. Other reports support the origin of PL to be defect related because different types of defects in the SiO2 (i.e. nonbridging oxygen hole centers or NBOHC) can emit visible PL around 2.3 eV [10]. When Si is partially oxidized, the energy band gap of nonstoichiometric SiOx varies in the range of 1.7 - 2.3 eV depending on the oxygen composition [11]. The PL peak around 2.1 eV may also arise due to some luminescent center at the interface between Ge nanoparticles and SiO2 matrix [12]. These reported results indicates that the visible PL can be due to quantum confinement effect in Ge nanoparticles or due to defects at the interface of nanoparticles / matrix or in the SiO2 matrix itself and exact origin of visible PL in the range of 2.0 - 2.3 eV is still debatable. Although time-resolved PL decay mechanism have been used to study excitation recombination process for Ge nanoparticles [7]. However it cannot provide any insight about the role of nanoparticles and nanoparticles-matrix interface electronic states. Hence the role
of Ge nanoparticles need to identify for the observed visible PL by investigating the effect of quantum confinement by removing (or minimizing) the effect of defects related effects.

In this Letter, Ge nanoparticles have been prepared by laser induced etching (LIE) technique to neglect the effect of substrate on the nanoparticles. The Ge nanoparticles prepared by this method are of the sizes comparable to Bohr excitonic radius of Ge (24.3 nm) [2]. The Ge nanoparticles, on extremely clean (no impurity) surface, generated in this way show visible PL at room temperature due to quantum confinement effect. This is supported by the calculation of radiative life time using the size of nanoparticles, which suggestes that quantum confinement effect plays the key role in room temperature visible PL from matrix free laser-generated Ge nanoparticles.

2 Experimental Details

To fabricate Ge nanoparticles, a Ge wafer was immersed in an aqueous solution of HF acid of 48 % concentration and irradiated with an argon-ion laser (514.5 nm). Details of the LIE set-up are given in the Ref. [13]. Different samples containing Ge nanoparticles of different sizes have been prepared by varying the etching time in the range of 35-55 minutes with a fixed laser power of 200 mW. After irradiation each of the samples was rinsed with ethanol and then dried before characterization. The PL spectra were recorded with a computerized spectroscopic system that consists of a SPEX double monochromator, a HAMAMATSU R943-02 photomultiplier tube. Samples were excited with photon energy of 2.41 eV from an argon-ion laser (COHERENT, INNOVA 90-5).
3 Results and Discussion

The AFM images in Figs. 1(a) -1(c) shows of time evolution of laser-etched Ge surfaces during LIE of Ge wafer. One important observation in Fig. 1 is the formation of smaller Ge nanoparticles for higher etching times. As etching time increases from 35 minute to 55 minute, Ge nanoparticles of a few nanometer can be seen in Fig. 1(c). These results predict that etching time is a controlling parameter to control the size and size distribution of Ge nanoparticle. The Ge nanoparticles generated in this method are formed directly on the Ge wafer itself. In this way the effect of matrix on PL can be neglected. Variation in the nanoparticle size as a consequence of increasing etching time can be understood as follows.

During LIE process, excess holes are generated when n-type Ge wafer is irradiated with laser light in the presence of HF acid solution. These laser-generated holes diffuse towards the surface due to an electric field produced by band bending at the Ge / electrolyte interface. The capture of holes at the surface leads to removal of Ge atoms leaving atomic size dip (pore) at the surface. Beale et al. [14], Lehmann and Gosele [15] have discussed that the pore formation over the surface change the electric field distribution in such a way that the holes focus to the bottom of pore. This leads to preferential etching at the bottom of the pores and etching will be faster in the substrate direction which leads to pyramidal structure over the surface. For the longer etching time the height of structure over the surface would become too long and incident light will not reach to the base. In this case etching at the top of structure will dominant and result in a gradual reduction of the height of the pyramidal structure as well as splitting of the structure, which leads to reduction of base diameter. As the nanoparticles over the surface becomes around 4 nm, quantum confinement effects cause an increase in the band gap [4,16]. Once the band gap has increased sufficiently, there is no absorption of photons i.e. there is natural stop for further etching due to band gap widening.
Possibility of quantum confinement effect in laser generated Ge nanoparticles has been investigated using PL spectroscopy. Fig. 2 shows the room temperature PL spectra from the assembly of Ge nanoparticles prepared using different etching times. The comparisons of PL spectra for different irradiation time indicate that the observed PL ranges from 2.0 - 2.2 eV. Various models [4,5,8, 10-12] have been proposed to explain this type of observed PL. The visible PL is attributed either to quantum confinement of excitons or to be originating from defects at the nanoparticles/ matrix interface or in the matrix itself. However, the quantum confinement effects can explain the majority of the observed PL [3,5,18], while in some cases, other mechanism also contributes in addition to the quantum confinement effect [5]. In the present study, the nanoparticles are grown (in isolation) directly over the Ge wafer without any matrix, i.e. the matrix and interface effect is excluded and should have no effect on observed PL. The LIE process has involvement of fluorine or hydrogen, so there species such as GeF$_4$, GeHF$_4$ or H$_2$GeF$_6$, can form a passivation layer over the surface and may generate recombination centers for the carriers, where PL may come due to chemisorbed molecules over the surface [19]. Thus, it is important to exclude the effect of chemical species to see the sole contribution of quantum confinement in the observed PL. Samples were rinsed with ethanol to remove the etch products from the surface of nanoparticles before recording the PL spectra. Thus, the only possible expected origin for visible PL is the quantum confinement of excitons.

Comparison of PL spectra in Fig. 2(I) for different irradiation times indicates that as irradiation time increase from 35 to 45 minute there is a strong increase of the PL intensity with an emission band around 2.1 eV. As irradiation time increases to 55 minutes (Fig. 2(c)) the peak position of band shifts to 2.2 eV. Thus, a blueshift of around 1.5 eV is observed for the Ge nanoparticles in comparison to the bulk Ge. The blueshift of the PL peak is
attributed to the quantum confinement effect in very small nanoparticles. The broadening of the peak is associated with the particle size distribution. For 35 minute irradiation time no strong PL is observed because quantum confinement effect are only significant when size is comparable to Bohr radius of the excitons. For irradiation time of 45-55 minute the blueshift of PL is observed due to enhancement of band gap caused by quantum confinement, as size is comparable to Bohr excitonic radius [2].

To investigate the range of nanoparticles which contribute efficiently to visible PL the size and size distribution are estimated using quantum confinement model proposed by Yorikawa et al. [20] by the fitting of PL spectra for irradiation time of 45 minute. With the assumption that the each particle has a very sharp luminescence the PL intensity for the ensemble of particles having a Gaussian distribution \([D(R_E)]\) of sizes can be written as

\[
S(E) = C\alpha(E_{exc} - E)D(R_E)\frac{R_E}{n \frac{E - E_g^0}{E_{exc} - E_g^0}}
\]

where \(R_E\) is the radius of nanoparticles defined by \(R_E = \left(\frac{\beta}{E - E_g^0}\right)^\frac{1}{n}\) The \(E_g^0 = 0.67\) eV is the gap energy of bulk Ge and \(n\) is 2 for 2D quantum confinement with \(\beta\) as the coupling constant. Two Gaussian distributions of sizes are used in the Eq. (1) to fit the experimental data. Doted lines in the Fig. 2(II) display theoretical PL spectrum for both Gaussian distributions. Continuous lines shown in the Fig. 2(II) is the superposition of two PL spectrums with two different size distributions. All fitting parameters and size distribution used for the line shape fitting of the PL spectrum are shown in the Table-1. These parameters reveal that the experimental PL data is the combination of two bands. The band-A at 1.80 eV is due to the nanoparticles of average size of 4.5 nm where the size distribution is in the range of 3.2 - 6 nm. The band-B at 2.10 eV is due to nanoparticles of average size of 4 nm with size distribution of 3.2 - 4.8 nm. This is in consonance with the results of Takagahara et al.
where luminescence peak energy of 2.18 eV corresponds to the quantum dot of average diameter of 4.2 nm. Y. Maeda [3] and P. K. Giri et al. [5] also observed the similar peaks in favour of the quantum confinement model. On the basis of observed results, we conclude that the dominant contribution to PL in the range of 2.0 - 2.2 eV comes due to confinement in smaller nanoparticles, and not related to defects at the nanoparticles/matrix interface or in the SiO$_2$ matrix itself.

The size dependent blue shift of the PL peak position and significant increase in the PL intensity with decrease in size indicates that the overall quantum efficiency has also increases [21]. This attributes to the transition from the indirect to direct recombination process that causes the increase in oscillator strength ($f_{osc}$) and it leads to reduction in the radiative lifetime ($\tau_R$) of carriers from few microseconds to few nanoseconds [21-23]. Theoretically the $f_{osc}$ and the lifetime $\tau_R$ for dipole-allowed optical transitions are calculated by the following simplified equation [24]:

$$\tau_R = \frac{2\pi\varepsilon_0 mc^3}{e^2 n\omega^2 f_{osc}} \approx 1.87 \times 10^3 \left( \frac{\lambda^2}{nf_{osc}} \right)$$

In the above equation we have use the exciton mass ($m = m_e + m_h$) with $m_e = 0.082m_0$ and $m_h = 0.043 m_0$ after Y. Maeda et al [2], where $m_0$ is the rest mass of electron. Here $\tau_R$ is in sec if $\lambda$ is expressed in meter. The effect of the change in oscillator strength with particle size ‘$d$’ has been addressed by Khurgin et al. [25] who have expressed the variation of $f_{osc}$ with ‘$d$’ by the following equation:

$$f_{osc} \approx \left[ \frac{\sin \left( \frac{0.86\pi d}{a} \right)}{\left[ 1 - \left( \frac{0.86\pi d}{a} \right)^2 \right] \left[ \left( \frac{0.86\pi d}{a} \right) \right]} \right]^2$$

where $a = 0.565nm$ is the lattice constant of crystalline Ge. For the smaller dimensions of
the nanoparticles the ‘f$_{osc}$’ can be approximated by power law of ‘d’ as follows

\[ f_{osc} \approx d^{-\gamma} \]  

(4)

where $\gamma$ is taken to be 6, Hybertsen and Needels [26] also suggested the $\gamma = 6$, whereas Sanders and Chang proposed a value of 5 [27]. The variation of the $f_{osc}$ with particle size $d$ (in the range of 1 -20 nm) for both the values of $\gamma$ is plotted in Fig. 3. It can be seen that for particle size greater than 10 nm the $f_{osc}$ is the order of $10^{-6}$ in both the cases. However, for particle size below 3 nm (which is the minimum calculated size for irradiation time of 45 minutes, Table-1) the $f_{osc}$ increases over several order of magnitude and reaches unity for particle size $d = 1$ nm. The Ge nanoparticles of 3 nm have $f_{osc}$ equal to $10^{-3}$ and $\lambda$ as 596 nm [emitted wavelength for irradiation time 45 minute], which gives radiative lifetime $\tau_R$ comes to be equal to 160 nm using Eq. (2). The radiative life time in the range of nanometer suggests that the PL is not due to defect related effects, where the life times are in the range of micrometers. The calculated results are in close agreement with the experimental predicted radiative lifetime for smaller Ge nanoparticles [5]. Thus the observed PL from laser-generated Ge nanoparticles are solely due to quantum confinement effect.

4 Conclusions

In summary, PL studies on defect free laser generated Ge nanoparticles have been done to see the sole effect of quantum confinement effect on electronic states in low dimensional Ge. Size dependent blue-shift in PL peak position with decreasing size has been attributed solely to the quantum confinement effect. The effect of defect and other possible contributions in visible PL has been neglected by fabricating the Ge nanoparticles on the Ge wafer itself. The
PL peak position shifts from 2.05 eV to 2.2 eV on decreasing the size of Ge nanoparticles due to quantum confinement and is not related to defects at the nanoparticles/matrix interface. In addition to this oscillator strength, $f_{osc}$ has also been calculated as a function of particle size, which has been used to calculate the radiative lifetime. The theoretically calculated lifetime comes out to be 160 ns as expected from confinement effect.

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Table 1: PL fitting parameters of band A and band B for the laser-etched Ge nanoparticles used in Eq.(1)

| Band | PL peak position(eV) | L(nm) | σ(nm) | L₁(nm) | L₂(nm) |
|------|----------------------|-------|-------|--------|--------|
| A    | 1.8                  | 4.5   | 0.24  | 3.2    | 6      |
| B    | 2.1                  | 4.0   | 0.12  | 3.2    | 4.8    |
Figure 1: AFM images of laser-etched Ge for different etching times of (a) 35 minute, (b) 45 minute and (c) 55 minute with fixed laser power of 200 mW.
Figure 2: (I) PL spectra from the assembly of Ge nanoparticles at different irradiation times of (a) 35 minute, (b) 45 minute and (c) 55 minute. (II) theoretical fitting of PL spectrum for irradiation time of 45 minute by confinement model. The theoretically calculated PL spectra using Eq. (1) is shown by dotted lines.
Figure 3: Oscillator strength, $f_{osc}$ as a function of particles size calculated from Eq.(4) for two different values of $\gamma$. 