Electron spin resonance study of defects in $Si_{1-x}Ge_x$ alloy nanocrystals embedded in SiO_2 matrices: Mechanism of luminescence quenching

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Dangling bond defects in $Si_{1-x}Ge_x$ alloy nanocrystals (nc-$Si_{1-x}Ge_x$) as small as 4 nm in diameter embedded in SiO_2 thin films were studied by electron spin resonance (ESR), and the effects of the defects on photoluminescence (PL) properties were discussed. It was found that the ESR spectrum is a superposition of signals from Si and Ge dangling bonds at the interfaces between nc-$Si_{1-x}Ge_x$ and SiO_2 matrices (Si and Ge P_b centers). As the Ge concentration increased, the signal from the Ge P_b centers increased, while that from the Si P_b centers was nearly independent of Ge concentration. The increase in the number of Ge P_b centers was accompanied by strong quenching of the PL. The observed correlation between the two measurements suggests that the Ge P_b centers act as efficient nonradiative recombination centers for photogenerated carriers, resulting in the quenching of the main PL. [DOI: 10.1063/1.1362410]

I. INTRODUCTION

In recent years, nanometer-sized Si and Ge crystals (nc-Si and nc-Ge) have been extensively studied because they offer new possibilities for indirect band gap semiconductors as new materials in photoelectric applications. It has been demonstrated that the photoluminescence (PL) energy of nc-Si is tunable from the bulk band gap to the visible region by simply controlling the size.[1–6] This wide tunability of PL energy indicates that the PL is due to the recombination of excitons confined in zero-dimensional Si quantum dots. The tuning range can be expanded by $Si_{1-x}Ge_x$ alloy formation. In a bulk $Si_{1-x}Ge_x$ alloy, it is well known that Si and Ge resolve each other over the entire concentration range, and the band gap energy changes from a Si one to a Ge one when the concentration is changed. Similar effects have been successfully observed in nanometer-sized $Si_{1-x}Ge_x$ alloy crystals (nc-$Si_{1-x}Ge_x$);[7,8] the band gap energy (luminescence energy) of nc-$Si_{1-x}Ge_x$ changes from the widened band gap of nc-Si to that of nc-Ge as the Ge concentration increases.[7]

The other advantage of $Si_{1-x}Ge_x$ alloy formation is the breakdown of the k-conservation rule and the enhancement of the oscillator strength due to the violation of the translational symmetry of the crystalline lattice. In pure nc-Si, it has been demonstrated that the indirect band gap nature of bulk Si crystals is preserved even for nc-Si several nanometers in diameter, although the probability of the no-phonon optical transition is much larger than that of bulk crystals.[9] The indirect band gap nature results in a relatively long PL lifetime, which is one of the obstacles to realizing Si-based light-emitting devices. In our previous work on resonant PL from nc-$Si_{1-x}Ge_x$, we demonstrated that the structures corresponding to the momentum conserving phonons are smeared out by increasing the Ge concentration.[8] Furthermore, shortening of the radiative lifetime with increasing Ge concentration has been commonly observed.[8,10,11] These results provide strong evidence that the oscillator strength of nc-Si is greatly improved by $Si_{1-x}Ge_x$ alloy formation.

However, in actual nc-$Si_{1-x}Ge_x$, the luminescence efficiency is smaller than that of pure nc-Si.[7] One of the possible explanations for the low PL efficiency is the generation of defects caused by alloying at the interfaces between nc-$Si_{1-x}Ge_x$ and SiO_2 matrices, and the defects act as nonradiative recombination centers. Although some kinds of defects have been reported to exist at the interface between the $Si_{1-x}Ge_x$ alloy and their oxide,[12,13] it has not yet been clarified which defects act mainly as nonradiative recombination centers. In order to make good use of the advantages of the nc-$Si_{1-x}Ge_x$ mentioned, detailed studies on the mechanism of PL quenching are indispensable.

In this work, we prepared nc-$Si_{1-x}Ge_x$ as small as 4 nm in diameter embedded in SiO_2 thin films with different Ge concentrations and studied the electron spin resonance (ESR) and PL properties. It will be shown that both properties depend on the Ge concentration. From a comparison between these two measurements, we will discuss the mechanism of PL quenching.

II. EXPERIMENT

$Si_{1-x}Ge_x$ alloy nanocrystals were prepared by the same method used in our previous work.[7,8] Si, Ge, and SiO_2 sputtering targets were simultaneously sputtered in Ar gas of 0.3 Pa using a multitarget sputtering apparatus. The substrates were fused quartz plates. The thickness of the films for PL and ESR measurements were about 700 nm and 8.4 μm, respectively. Ge concentration in the films was controlled by changing the rf power and the distance between the substrate

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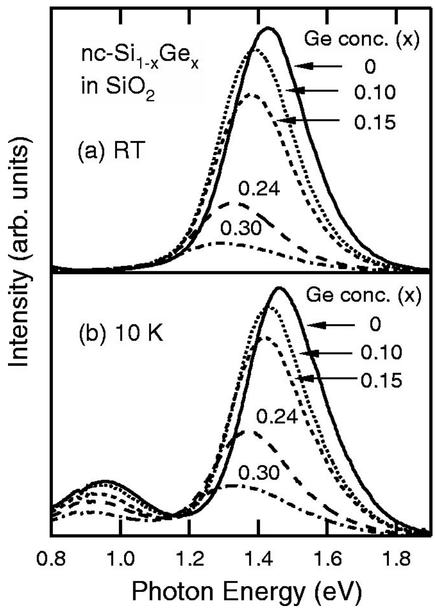

FIG. 1. PL from nc-$Si_{1-x}Ge_x$ dispersed in SiO_2 thin films (a) at room temperature and (b) at 10 K. Ge concentration is changed from 0 to 0.30.

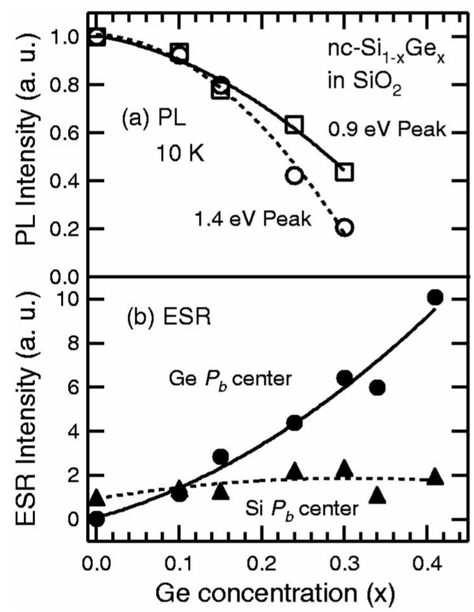

FIG. 2. (a) PL intensities of the 1.4 and 0.9 eV peaks at 10 K, and (b) the integrated intensities of the ESR signals from Si and Ge P_b centers as a function of Ge concentration.

and the target during cosputtering. After the deposition, films were annealed in a N_2 gas atmosphere for 30 min at 1100 °C. During the annealing, nc-$Si_{1-x}Ge_x$ were grown in SiO_2 matrices. Ge concentration (x) was changed from 0 to 0.41. The values of x were determined from Raman spectra.[7,14] The size of nc-$Si_{1-x}Ge_x$ was estimated by cross sectional high-resolution transmission electron microscopic (HRTEM) observations. HRTEM observations revealed that spherical nanocrystals as small as 4–5 nm in diameter were grown in amorphous SiO_2 matrices. Each nanocrystal was isolated from the others by SiO_2 barriers several nanometers in thickness. The PL spectra were measured with a single monochromator equipped with a liquid N_2 cooled Ge detector (0.8–1.9 eV) and a liquid N_2 cooled InSb detector (0.4–0.8 eV). The excitation source was the 488.0 nm line of an Ar ion laser. The PL spectra were measured in the temperature range between 10 and 300 K in a continuous-flow He cryostat. X-band ESR was measured with a conventional ESR spectrometer at room temperature. The intensity of ESR signals was calibrated by simultaneously measuring the signal from a fixed amount of Mn^{2+}/MgO powder.

III. RESULTS

Figure 1(a) shows the room temperature PL spectra of nc-$Si_{1-x}Ge_x$ with various Ge concentrations. For the sample with $x=0$ (pure nc-Si), a PL peak is observed around 1.43 eV. This PL arises from the recombination of electrons and holes confined in nc-Si.[3,4] We can see that, as the Ge concentration increases, the PL peak shifts to lower energies and reaches 1.29 eV for the sample with $x=0.30$. This shift is accompanied by the quenching of the PL by about one order of magnitude. By further increasing the Ge concentration, PL was completely quenched. Figure 1(b) shows the PL spectra at 10 K. In addition to the main PL band, an additional PL peak is observed around 0.9 eV. The 0.9 eV peak is generally assigned to the recombination of photoexcited carriers via Si dangling bonds at the interfaces between nc-Si and SiO_2 matrices (Si P_b centers).[15–18] The intensity of this peak shows the same Ge concentration dependence as that of the main band. The integrated PL intensities of the 0.9 and 1.4 eV peaks at 10 K are shown in Fig. 2(a) as a function of Ge concentration. Both the peaks become weaker at almost the same rate by increasing Ge concentration.

Figure 3 shows the ESR derivative spectra of nc-$Si_{1-x}Ge_x$ with various Ge concentrations. For pure nc-Si, a sharp ESR signal is observed; the g value and the peak-to-peak linewidth are 2.0055 and 10 G, respectively.

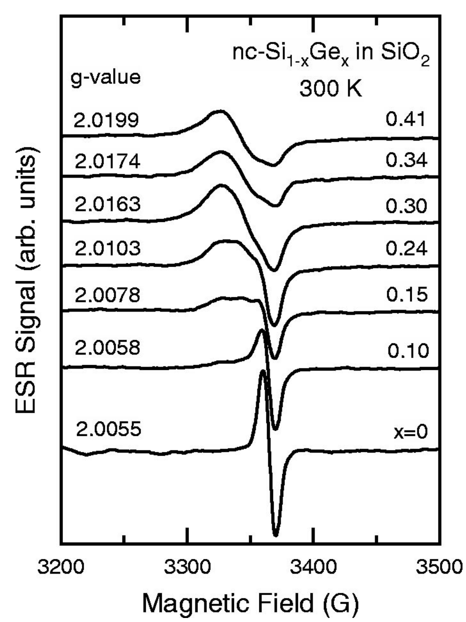

FIG. 3. ESR derivative spectra of nc-$Si_{1-x}Ge_x$ dispersed in SiO_2 thin films at room temperature. Ge concentration is changed from 0 to 0.41.

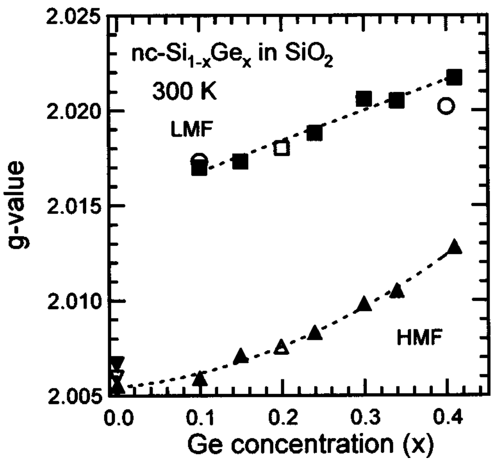

FIG. 4. g values of the HMF (▲) and LMF (■) signals as a function of Ge concentration. The data for Si P_b centers [△ (Ref. 12), ▽ (Ref. 16), and ▼ (Ref. 19)] and Ge P_b centers [□ (Ref. 12), and ○ (Ref. 13)] are also plotted. The broken curves are drawn to guide the eyes.

This signal can be assigned to Si P_b centers.[16,19] For pure nc-Si, a clear correlation has been observed between the intensity of this signal and that of the 0.9 eV PL.[16] For the sample containing Ge atoms, in addition to the signal from Si P_b centers, a broad signal appears at the low-magnetic-field side (LMF) (e.g., $x=0.24$). The intensity of the broad signal increases as the Ge concentration increases. For the sample with $x=0.41$, the g value and the peak-to-peak linewidth of the broad signal are 2.0199 and 47 G, respectively.

IV. DISCUSSION

A. Origin of the ESR signal

Although the observed ESR spectrum apparently consists of more than two peaks, we tentatively deconvoluted the ESR spectrum into two components. All the spectra could be well deconvoluted by two Lorentzian functions. Figure 4 shows the g values of the high magnetic field side (HMF) signal and the LMF signal as a function of Ge concentration. The broken curves are drawn to guide the eyes. By increasing the Ge concentration, the g values of both signals increase. For comparison, we plotted the data for Si P_b centers and Ge P_b centers from the literature on surface oxidized porous $Si_{1-x}Ge_x$,[12] an oxygen implanted $Si_{1-x}Ge_x$ layer,[13] surface oxidized porous Si,[19] and nc-Si in SiO_2 prepared by a cosputtering method.[16] We can see that the present results agree well with the previous results, suggesting that the HMF and LMF signals can be assigned to Si and Ge P_b centers, respectively.

Since Si and Ge are mixed with each other randomly, each signal is assumed to consist of four components due to the difference in the arrangement of back-bond atoms. The signals from Si P_b centers consist of $-Si{\equiv}Si_3$, $-Si{\equiv}Si_2Ge$, $-Si{\equiv}SiGe_2$, and $-Si{\equiv}Ge_3$, while those from Ge P_b centers consist of $-Ge{\equiv}Si_3$, $-Ge{\equiv}Si_2Ge$, $-Ge{\equiv}SiGe_2$, and $-Ge{\equiv}Ge_3$. Since the spin–orbit coupling constant of Ge (940 cm^{-1}) is larger than that of Si (142 cm^{-1}) by a factor of 7, as the number of Ge atoms at the back-bonding sites increases, the g value of a dangling bond becomes larger.[13,20] Therefore, the observed increase in g values with Ge concentration indicates that the number of P_b centers with a larger number of Ge back bonds increases with Ge concentration.

Another factor that might be taken into account is the narrowing of the band gap with increasing Ge concentration. It is expected that the g values of the Si and Ge P_b centers would increase by narrowing the band gap because the deviation of the g value from that of a free electron is inversely proportional to the band gap of a $Si_{1-x}Ge_x$ alloy.[20,21] However, this effect is generally much smaller than that discussed above, so it is considered negligible.

B. Correlation between ESR and PL

The integrated intensities of the ESR signals from Si and Ge P_b centers are plotted in Fig. 2(b). The ESR intensity of the Ge P_b centers increases with Ge concentration, while that of the Si P_b centers is nearly independent of Ge concentration, indicating that the number of Ge P_b centers increases, while that of Si P_b centers is constant. We can see in Fig. 2 that the increase in the number of Ge P_b centers is associated with the quenching of the PL, suggesting that the increase in the number of Ge P_b centers is responsible for the PL quenching.

In Fig. 2(a), not only the main PL band but also the 0.9 eV PL becomes weaker. As mentioned above, the 0.9 eV PL is assigned to the recombination of photoexcited carriers via Si P_b centers. For pure nc-Si, a clear correlation has been observed between the PL intensity and the intensity of the ESR signal from Si P_b centers; the intensity of the 0.9 eV PL is nearly proportional to that of the ESR signal of Si P_b centers.[16] Similarly, for nc-$Si_{1-x}Ge_x$, it is expected that the intensity of the 0.9 eV PL shows the same Ge concentration dependence as that of the ESR signal from Si P_b centers. However, in Fig. 2(b), in spite of the constant intensity of the signal from the Si P_b centers, the 0.9 eV PL becomes weaker with Ge concentration. This result suggests the following model for PL quenching by $Si_{1-x}Ge_x$ alloy formation. Ge P_b centers form defect levels in the band gap of nc-$Si_{1-x}Ge_x$. The levels are deeper in energy than those of Si P_b centers. Photoexcited electron–hole pairs in nc-$Si_{1-x}Ge_x$ are trapped at the Ge P_b centers and recombine via the centers, if there is at least one Ge P_b center in a single nanocrystal. The recombination is made nonradiatively at temperatures higher than 10 K, because no PL signal was detected in the range between 0.4 and 0.8 eV. Under this assumption, nc-$Si_{1-x}Ge_x$ in a sample can be classified into three categories. One is nc-$Si_{1-x}Ge_x$ which do not have any P_b centers. These nanocrystals show a band edge PL around 1.4 eV. The second kind of nanocrystals are those having at least one Si P_b center but no Ge P_b center. Since the lifetime of the band edge PL is very long (several tenth of μs to ms),[5,8,22] photoexcited carriers in these nanocrystals are always trapped at the Si P_b centers. Therefore, these nanocrystals do not show a band edge PL but only the 0.9 eV PL. The last kind of nanocrystal are those containing at least one Ge P_b center. In these nanocrystals, despite whether there exist Si P_b centers, photoexcited carriers always recombine via Ge P_b centers. The observed PL spectra are an ensemble of those from these three kinds of nanocrystals. As the Ge concentration increases, the ratio of nanocrystals having Ge P_b centers increases, resulting in the quenching of both the main PL and the PL from Si P_b centers.

For pure nc-Si, passivation of dangling bond defects by hydrogen and oxygen has been reported to be effective in improving luminescence efficiency.[23,24] Recently, we demonstrated that doping of P atoms into SiO_2 films containing nc-Si brings about drastic improvement in the PL of nc-Si.[15,16] Similarly, for nc-$Si_{1-x}Ge_x$, passivation of Ge P_b centers by similar approaches might be possible. These studies are now underway in our laboratory.

V. CONCLUSION

The dangling bond defects in nc-$Si_{1-x}Ge_x$ embedded in SiO_2 matrices were studied by ESR, and the correlation of the defects with the PL properties was revealed. It was found that the ESR spectrum is a superposition of signals from Si and Ge P_b centers. The signal from the Ge P_b centers increased with the Ge concentration, while that of the Si P_b centers was nearly independent of Ge concentration. By increasing the number of Ge P_b centers, the PL intensity was strongly quenched. From the observed clear correlation between the two data, it can be concluded that Ge P_b centers act as efficient nonradiative recombination centers for photogenerated carriers, resulting in the quenching of the main PL.

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