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Luminescence in selectively excited germanium microcrystallites

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We have obtained the luminescence spectrum from Ge microcrystallites selectively excited. The spectrum has a broad feature with several structures, which are classified into two categories: a steplike structure near the excitation energy with an onset energy of 23 meV that is assigned to the phonon structure due to the LA(L) phonon, and a feature with three peaks at larger energy shifts (220, 380, and 590 meV) from the excitation energy. The results suggested a close similarity of the luminescence mechanisms of the Ge microcrystallite system and porous Si. [S0163-1829(97)51528-1]

Recently, there has been increasing interest in visible luminescence from microcrystallites of indirect gap semiconductors, such as Si or Ge. Since the discovery of efficient visible region luminescence in porous silicon,[1] a number of reports have appeared on its luminescent properties, both in static and dynamic measurements.[2]

As for the Ge microcrystallites, there are relatively few reports. Maeda and co-workers have reported visible luminescence from Ge microcrystallites prepared by co-sputtering.[3] Paine and co-workers have observed visible luminescence from Ge microcrystallites.[4] They grew the $Si_{1-x}Ge_x$ alloy on Si substrate by chemical vapor deposition and oxidized it to a GeO_2-SiO_2 layer in high-pressure dry O_2 or steam, then reduced it with H_2 to make Ge microcrystallites in a SiO_2 matrix. However, it is not easy to find the conditions for reproducing samples that emit visible light using the former method, while the latter method requires highly sophisticated equipment and procedures. The development of research on Ge microcrystallites, therefore, is less remarkable than work on porous silicon.

The sol-gel method has been providing a more practical approach for preparing semiconductor microcrystallites. There are many reports of preparing CdS, PbS, CdTe, CdSe, and CuBr (Ref. 5) microcrystallites embedded in glass using this method. Recently, Nogami and co-workers reported that they have prepared the Ge microcrystallites in glass by the sol-gel method and observed visible luminescence from them.[6] Using this method, samples showing visible luminescence can be reproduced easily with relatively simple equipment and processes.

In general, it is difficult to prepare microcrystallites of controlled size. Thus, available microcrystallites systems are usually so inhomogeneous that the luminescence spectra from them are broad. Therefore, selective excitation spectroscopy is a powerful method for extracting individual information, eliminating the effect of spectrum broadening due to inhomogeneity. In CuCl microcrystallites embedded in alkali halides, the luminescence from those of a certain size was studied. In porous silicon, phonon structures were observed in the luminescence spectra under selective excitation.[7,8].

To investigate the optical properties of the Ge microcrystallites, we applied the selective excitation method to systems prepared by the sol-gel method.

We prepared the germanium microcrystallites in silica glass by the method described by Nogami and co-workers. A block of the SiO_2-GeO_2 glass was prepared by the sol-gel method and dried for 6 days. Then it was reduced for 2 h at 700 °C under a flowing 20%H_2–80%N_2 gas mixture to form Ge microcrystallites in this glass matrix.

The luminescence was measured in a flow-type He cryostat in He atmosphere. For the excitation, we used an Ar ion laser and a cw dye laser with Rhodamine 6G. The signal was analyzed by an 85 cm double monochromator (SPEX 1402) and detected by a photon-counting technique using a GaAs photomultiplier (Hamamatsu 943-02). All the spectra were corrected by reference to a tungsten standard lamp.

In the luminescence excitation measurement, the excitation source was the light from a Xe-arc lamp dispersed by a single monochromator.

In the radiative lifetime measurements, we used two kinds of light sources for excitation. One was a dye laser (Rhodamine 6G) synchronously pumped by the second harmonic light of a cw mode-locked Nd-yttrium-aluminum-garnet (YAG) laser, the other was the sum frequency light of the dye laser and the YAG laser obtained by a LIO (lithium iodate) crystal. The repetition rate of the laser was 82 MHz. The luminescence was analyzed by a 50 cm single monochromator (NARUMI model RM21). The spectrally resolved temporal behavior of the luminescence was analyzed with a combination of a synchro-scan streak camera (Hamamatsu model C1587) and a charge-coupled device camera.

The luminescence spectra of Ge microcrystallites under various excitation wavelengths (4579, 4765, 4880, 5907, and 6092 Å) at 4.2 K are shown in Fig. 1. Each spectrum has a broad feature with several structures. The high-energy side of the luminescence spectrum is limited by the excitation photon energy; the intensity of the anti-Stokes component is practically zero at 4.2 K. The low-energy side seems to be limited always around the same energy, regardless of the excitation photon energy. Thus, the bandwidth decreases as the excitation photon energy decreases. This behavior is reminiscent of the behavior of the inhomogeneously broadened luminescence band in porous silicon. The shape of the luminescence spectrum seems to reflect an inhomogeneous distribution of luminescent energy levels. In the theoretical calculation using effective-mass approximation,[9] this luminescence energy range corresponds to the microcrystallite size of 36–54 Å.

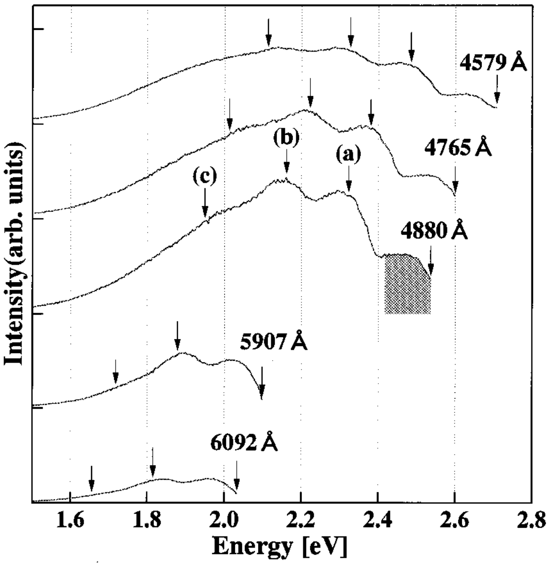

FIG. 1. Luminescence spectra under various excitation wavelengths (4579, 4765, 4880, 5907, and 6092 Å). We assigned energy shifts of the peaks (a), (b), and (c) from the excitation energy as 220, 380, and 590 meV in the luminescence spectrum under 4880 Å excitation assuming Gaussian shapes.

The structures in the spectra are sorted into two categories: the steplike structures near the excitation energy (the shaded area in the spectrum under 4880 Å excitation in Fig. 1) and the three peaks at larger energy shifts from the excitation energy [arrows (a), (b), and (c) in Fig. 1].

First, we discuss the former structure. Figure 2(a) shows the luminescence spectrum near the excitation energy. In this spectrum, there are steplike structures near the excitation energy under 4880 Å excitation at 4.2 K. In our sample, these structures appear under any excitation wavelength shorter than 5200 Å. To see these step structures clearly, we calculated the second derivative of the luminescence spectra since it will show maxima exactly at the onset energies of the steps where the slope abruptly increases.[10] As indicated in Fig. 2(b), it shows a clear maximum at about 23 meV from the excitation energy, which corresponds to the onset energy of the structure.

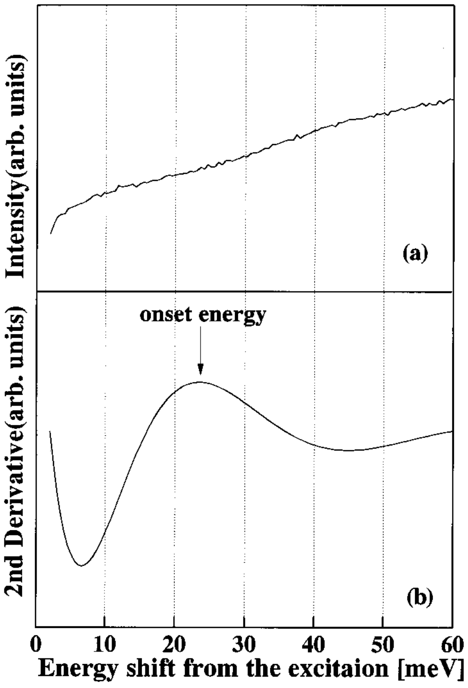

FIG. 2. (a) Luminescence spectrum under 4880 Å excitation, corresponding to the shaded area in Fig. 1. (b) The second derivative of the curve (a).

Suemoto and co-workers have observed similar steplike structures near the excitation energy in the luminescence spectrum of porous Si excited selectively and interpreted them in the following way.[7] In porous Si the onset energy is about 61 meV. Assuming 4 meV for singlet-triplet splitting,[8] the residual energy 57 meV is close to the transversal optical phonon at the X point in the Brillouin zone. They discussed the possibilities of two alternative models based on recombination luminescence accompanied by optical phonons. One is to assume fine structures in the luminescence spectrum for each microcrystallite. If the microcrystallites of the same size are selectively excited, these fine structures will appear in the luminescence spectrum. The other model assumes fine structures in the luminescence excitation spectrum for each microcrystallite. Supposing that the luminescence from each particle produces a very sharp line and that the inhomogeneous distribution is nearly flat, an inverted excitation spectrum should appear in the luminescence spectrum under monochromatic excitation. In the former model, however, the structure will appear as discrete lines at intervals of the phonon energy, which cannot explain the steplike structure observed in porous Si. They consequently assumed the latter model. In the luminescence spectrum of Ge microcrystallites, the steplike structures we observed had shape and behavior similar to those porous Si. We, therefore, assume the model in which these steplike structures reflect mainly the luminescence excitation spectrum from each microcrystallite.

In the optical absorption spectrum of bulk Ge, Macfarlane and co-workers found steplike structures near the optical-absorption edge.[11] Since Ge is an indirect-gap semiconductor, the optical transition requires the creation or annihilation of phonons for crystal momentum to be conserved. They concluded that these steplike structures corresponded to phonon-assisted optical absorption.

As the candidates involved in the optical transition, we can suppose several phonon energies at critical points on the phonon-dispersion curves, which were either measured by neutron scattering[12] or calculated from lattice dynamics.[13] The energies are 37.2 meV for the degenerated optical phonon at the Γ point, 33.8 meV for the TO phonon at the X point, 7.8 meV for the TA phonon and 27.6 meV for the LA phonon at the L point. In our case, the onset energy is about 23 meV, which is near the last value. In fact, the steplike structures corresponding to the LA phonon at the L point was observed in the optical-absorption spectrum of bulk Ge.[11] It is, therefore, highly possible that the steplike structures we observed correspond to the optical-transition process with the LA phonon mode at the L point. Similarly, the TO phonon at the X point contributes in porous Si (Refs. 7 and 8) and the bulk system.[14]

The existence of the above-mentioned steplike structures is common to both the microcrystalline and the bulk Ge. However, we can notice differences between their spectra in the following two aspects. One is the existence of no-phonon transition in Ge microcrystallite. In the bulk Ge, no-phonon transition is forbidden and not observed, while the luminescence component between the excitation energy and the onset of the one-phonon structure in the microcrystallites is ascribed to the no-phonon transition. The other is a slight difference in onset energies of the one-phonon assisted transition in Ge microcrystallites (23 meV) and in bulk Ge (27 meV).

The above common and different behaviors of the steplike structures can be explained by the symmetries in the bulk and microcrystallite Ge. Ge is a diamond structure, which is a face-centered lattice with a basis consisting of two Ge atoms. The translational symmetry of the primitive lattice brings the momentum-conservation law and the rotational symmetry of the basis defines the symmetry of the wave functions on the high-symmetry points and lines in the Brillouin zone. Therefore, we have strict selection rules in the ideal crystals. The following group theoretical analysis[15] can explain the existence of the absorption onset associated with the LA phonon at the L point in bulk Ge. In the energy band of Ge, the minimum in the conduction band occurs at the L point with symmetry L_1 whereas the maximum in the valence band occurs at the Γ point with symmetry $\Gamma_{25'}$. The indirect optical process from $\Gamma_{25'}$ to L_1 occurs through the virtual intermediate states to fulfill the momentum-conservation law. An electron in Γ_{25} can be excited radiatively to $\Gamma_{2'}$ and then scattered by a phonon from $\Gamma_{2'}$ to L_1, or it can be scattered first to $L_{3'}$ and then excited to L_1. The scattering part in the above processes decides which phonon mode assists the indirect transition. Applying the group theoretical considerations to the phonon scattering part, we obtain

$$L_1 \times \Gamma_{2'} = L_{2'}, \tag{1}$$

$$L_{3'} \times \Gamma_{25'} = L_{1'} + L_{2'} + 2L_{3'}. \tag{2}$$

The LA phonon at the L point has $L_{2'}$ symmetry and can assist the indirect transition in bulk Ge. However, the size of microcrystallites cannot be regarded as infinite. Even in a small system, the rotational symmetry of the basis and the translational symmetry in a short distance are expected to remain. This allows us to use the same energy band description as in bulk and the above-mentioned group theoretical analysis will still be valid in the microcrystalline systems.

However, the translational symmetry in a long distance is lost in such a small system and the momentum-conservation law will become loose. This partial breakdown of the momentum-conservation law is the reason for the existence of no-phonon transition. It also allows one-phonon transitions with acoustic phonons, which is not located exactly at the L point. This effect might shift the onset energy of the steplike structure from the LA phonon energy at the L point toward the energy of the density-of-states maximum on the acoustic-phonon dispersion curve. We can find that the density of phonon states has the maximum at 23 meV, near the middle point between the L and the K points on the dispersion curve. Thus we could understand the observed downward shift of the onset energy for the one-phonon structure.

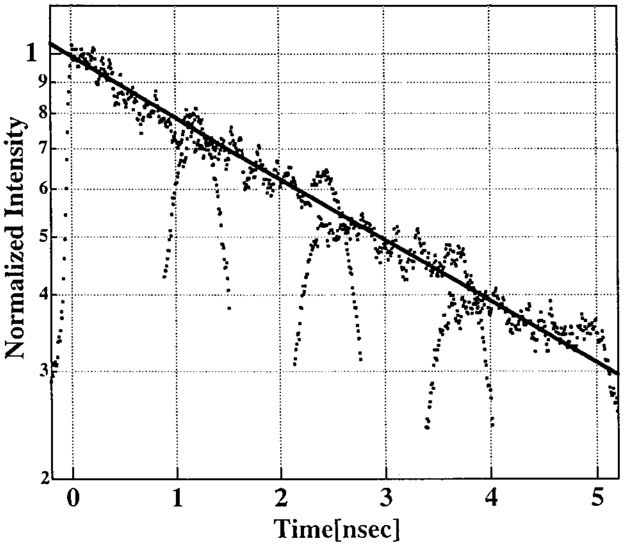

FIG. 3. The dots are the streak camera image at 4862 Å under 3900 Å excitation. Four frames with a width of 1.4 ns at different delays are superimposed in this figure. The curve is the single exponential decay with the lifetime 4.3 ns fitted to the dots.

Next, we discuss the three peaks (a), (b), and (c) in the luminescence spectrum as shown in Fig. 1. Nogami and coworkers have already found these peaks in the luminescence spectrum under 4880 Å excitation at liquid-nitrogen temperature. The positions of these peaks were the same for all the samples they examined. They concluded that these peaks were luminescence arising from microcrystallites with specific diameters. But by varying the excitation wavelength, we found that energies of these peaks moved in parallel with the excitation energy. Since the three peaks are always located at about 220, 380, and 590 meV from the excitation energy, they do not represent the luminescence from microcrystallites of specific diameters. This behavior might be understood as the Raman scattering corresponding to some elementary excitation. Thus we have measured the lifetime of these peaks with a streak camera. The excitation light wavelengths are 3900 and 5700 Å. We have obtained the streak images at various photon energies. Figure 3 shows the decay curve monitored at 4862 Å under 3900 Å excitation. The decay rate is 4.2±0.2 ns at various monitoring wavelengths for each excitation wavelength. These finite lifetimes of the signal indicate that we can discard the possibility of Raman scattering. We also obtained luminescence excitation spectra. In Fig. 4, the dots indicate the luminescence excitation spectrum monitored at 5145 Å; the solid line is the luminescence spectrum under excitation at the same wavelength. They are mirror images of each other at about 5145 Å. This result shows that the luminescence intensity monitored at a certain photon energy is determined basically by the difference between the monitor and the excitation photon energies. Thus the structures seen in both spectra can be regarded as peaks of energy loss between the excitation and recombination processes. The formation of the semiconductor nanostructure modifies the properties in the lattice vibration and the electronic structure. We can, therefore, consider vibrational and electronic origins for the energy loss corresponding to the observed structures in the following way.

As for the electronic origin, we can consider firstly the effect of relaxation between electronic states which appears as a result of the quantum size effect in microcrystallites. In

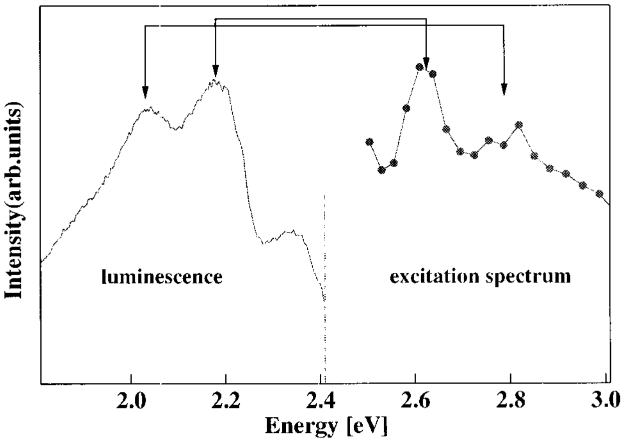

FIG. 4. The solid line is the luminescence spectrum excited by a 5145 Å line of an Ar laser, and the dots are the luminescence excitation spectrum monitored at 5145 Å.

this case, the energy shift is expected to depend critically on the size of the microcrystallite. The spacings of the peaks slightly decrease as the excitation energy is lowered. However, this decrease seems smaller than the size dependence expected from the quantum confinement effect. Also, we can consider the effect of the multivalley band structure including L and Γ. The direct gap at the Γ point is located 154 meV above the indirect gap at the L point in bulk Ge at 1.5 K.[16] This situation is reflected in the absorption spectrum near the absorption edge in the bulk crystal, that is, the indirect absorption with phonon assistance rises fairly slowly, whereas the absorption due to the direct gap rises quite rapidly at slightly higher energy. This abrupt rise in the absorption is observed at around 150 meV from the indirect edge.[17] If we can assume that this relative location at the Γ and the L point is conserved in the microcrystallites, this absorption profile might be reflected in the luminescence spectrum under selective excitation. Actually, the onset energy in the spectrum we observed is about 160 meV, which is close to this energy difference. The subsequent peaks at 380 and 590 meV require another explanation.

As for the vibrational origin, we can consider the Ge-H$_n$ ($n=1,2,3$) vibration sideband. In preparing this sample, we annealed the GeO_2-SiO_2 glass in H_2 atmosphere. It is, therefore, possible that hydrogen atoms terminate dangling bonds of Ge atoms on the surface of the microcrystallites and that the vibration of Ge-H$_n$ couples to the optical absorption or emission in Ge microcrystallites. They are the bond-stretching mode (about 240 meV), the bond-bending mode (about 100 meV), the wag mode (about 70 meV), and the rock mode (about 50 meV) in Ge-H$_n$.[18] The number of hydrogen atoms terminating a Ge atom makes a slight difference in the energy of the modes. Peak (a) is close to the energy of the bond-stretching mode. Peaks (b) and (c) might correspond to combinations of these modes.

In conclusion, we have obtained the luminescence spectrum from Ge microcrystallites excited selectively and observed two kinds of structures in the spectra. We assigned a steplike structure at 23 meV from the excitation energy to a phonon structure due to the LA phonon at the L point. We also proposed two possible interpretations for the other structure at a larger energy shift from excitation energy. Further experiments are in progress to further reveal the nature of these peaks in Ge microcrystallites.

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