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PHOTOLUMINESCENCE OF BULK Si-Ge SINGLE CRYSTALS

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Abstract. Single crystals of Si-Ge alloy in the composition range from 0 to 50 at.%Si were grown with traveling solvent method. The compositions of the above crystals were shown to be uniform with EPMA measurement. The band gap energy of the crystals increased linearly in the range from 0 to about 15 at.%Si and varied gradually above 15 at.%Si. In order to determine the dependence of the symmetry of conduction band minimum on Si composition, we measured photoluminescence spectrum under uniaxial stress along <111> direction considering the difference of symmetry of conduction band minimum in Ge and Si. The dependence of peak energy of excitonic no-phonon line on uniaxial stress along <111> direction changed at about 15 at.%Si. From these results, it was confirmed that conduction band minimum was on Ge-like L points (<111>) at composition up to 15 at.%Si and on Si-like near X points (bottom of Δ) (<100>) above 15 at.%Si.

Introduction

Si-Ge alloy forms a complete series of solid solution. Various properties of the alloy depend on Si composition. For example, the bandgap energy continuously varies from 0.74 eV(Ge) to 1.16eV(Si) as Si concentration increases[1-5]. It has been proposed that the conduction band minima change from Ge-like L points (<111>) to Si-like X points (bottom of Δ) (<100>) at about 15 at.%Si [6]. This proposal is supported by several experimental results, for example photoluminescence (PL) [3-5] and optical absorption [1,2] measurement.

To clarify above properties of Si-Ge alloy directly, it is relevant to measure photoluminescence under uniaxial stress, considering the difference of symmetry of conduction band minimum in Si and Ge. We show whether the symmetry of conduction band minimum of the alloy is Si-like or Ge-like at each alloy composition from above experiment.

Experiment

Single crystals of Si-Ge alloy were grown with traveling solvent method. The composition of those crystals were measured in the direction of growth axis with EPMA measurement after chemical polish with an etchant ($HF:HNO_3=5:1$) at 80°C for 30 seconds. The accelerating voltage of electron beam was 20kV and the beam size was 30 x 30 μm. The penetration depth of electron beam was estimated to be about 2 μm. The interval of the sampling points was 1mm.

The samples for PL measurement were cut to 1mm thickness from the grown crystals. They were chemically polished with the above etchant. We measured PL of above samples to determine the bandgap energy. Excitation was by the 514.5nm line of an Ar^+laser at 4.2K.

We cut out samples for the measurement of PL under uniaxial stress in dimensions 2x2x5mm, the longest side being parallel to [111] direction.

Results and Discussion

Grown crystal with traveling solvent method. Figure 1 shows Si-Ge single crystal grown by traveling solvent method. The grown crystals were confirmed to be single crystals or poly crystals with an etchant ($HF:H_2O_2:H_2O$=1:1:4) which was sensitive to grain boundary. The samples were n-type conductivity with free electron concentrations of the order of $10^{15}cm^{-3}$ at room temperature.

Uniformity of composition. Figure 2 shows the composition in the direction of growth axismeasured with EPMA. The abscissa shows the distance from the initial growth point. The composition was shown to be almost constant along growth direction, and also in the perpendicular section to growth axis.

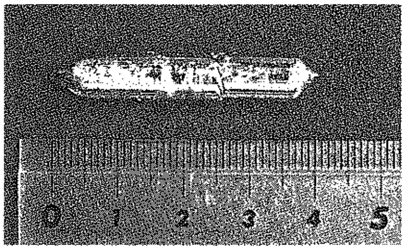


Fig. 1. Single crystal grown by traveling solvent method, whose composition is 26.2 at.%Si.

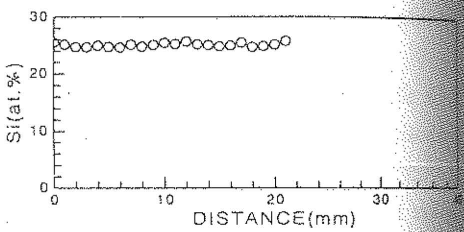


Fig. 2. Composition in the direction of growth axis with EPMA measurement.

Photoluminescence spectrum. Figure 3 shows the dependence of PL spectra on Si composition. NP in Fig. 3 indicates excitonic PL peak due to an exciton bound to shallow impurity, not assisted by phonon. Thus the peak energy of NP line is approximately regarded as bandgap energy. The spectra on the left side of NP line show excitonic luminescence spectra assisted by phonon, so called phonon replicas. Those phonon replicas are assigned to be Si-Si(TO), Si-Ge(TO), Ge-Ge(TO), Ge-Ge(LA) phonons from the left side according to the former works [4,5].

Figure 4 shows the dependence of peak energy of NP line on Si composition. It is shown that the bandgap energy increases linearly in the range from 0 to about 15at.%Si and increases gradually in the range above 15at.%Si. The above experimental result of NP line on Si composition x (at.%) was fitted by a least square procedure in the range from 0 to 15at.%Si. It is given as follows.

$$E(x)=0.012x+0.734 \text{ (eV)} \quad (1)$$

where E(x) is the peak energy of NP line. It is in agreement with following result reported by Weber and Alonso [5].

$$E(x)=0.0127x+0.74 \text{ (eV)} \quad (2)$$

Since free excitonic luminescence was measured in their experiment, the difference of constant terms (0.74 - 0.734 eV) above two equations corresponds to binding energy of an exciton to shallow donors. Free excitonic luminescence could not be detected in our experiment. This can be explained from the difference of carrier density of specimens, namely carrier density of their specimens was about one hundred times higher than that of our specimens at room temperature.

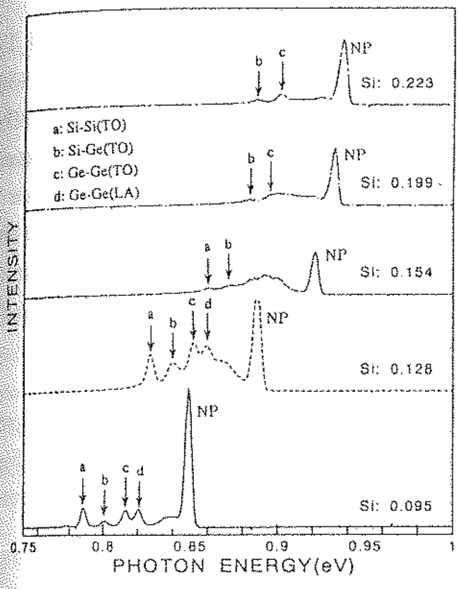


Fig. 3. The dependence of NP line on Si composition. NP line shows bound excitonic luminescence spectrum not assisted by phonon. The spectra on the left side of NP line are phonon replicas.

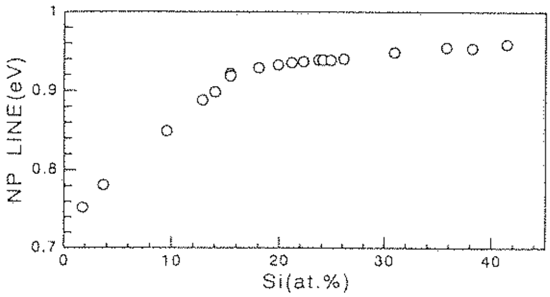


Fig. 4. The dependence of peak energy of NP line on Si composition.

Photoluminescence under uniaxial stress. As mentioned in the introduction, the symmetry of the conduction band minimum has been supposed to depend on the composition. In order to confirm this supposition directly, the dependence of PL peak position on the uniaxial stress were measured at various composition.

Equivalent four conduction band minima (<111>) and equivalent six conduction band minima (<100>) degenerate in Ge and Si, respectively. For uniaxial stress along <111> direction, the conduction band minima split into one and three equivalent conduction band minima in Ge, and not split in Si. The degenerate valence bands in Ge and Si are also removed into light hole and heavy hole bands at Γ point for uniaxial stress along <111> direction [7,8]. Hence, whether the conduction band minimum is Ge-like or Si-like can be determined in the investigation of the splitting of conduction band minima under uniaxial stress along <111> direction.

Figure 5 shows the dependence of peak energy of NP line on the stress. It remarkably changes around 15 at.%Si, being larger at low concentration (< 15at.%Si) than at high concentration (> 15at.%Si). The dependence on the stress at 24.3 at.%Si is similar to that of Si. This feature indicates that the conduction band minimum lies on <111> direction at low concentration (<15 at.%Si) and on <100> direction at high concentration (>15 at.%Si). Since these NP lines at low concentration up to 15 at.%Si shifts linearly to lower energy as the stress increases, these lines are related to a falling set of conduction band minima split in two sets under uniaxial stress along <111> direction. The weak dependence on the stress at high concentration more than 15 at.%Si is interpreted to be due to the decreasing of bandgap energy related to a rising light-hole band under hydrostatic component. PL spectrum related to a rising conduction band minimum under uniaxial stress along <111> direction was not detected in our experiment. One reason is probably that the higher luminescence energy related to a rising conduction band minimum is used to excite electrons from valence band to a falling conduction band minimum.

Figure 6 shows the dependence of peak energy of NP line on the stress at about 15 at.%Si. The dependence is different from that of low concentration (<15at.%) and high concentration (>15at.%Si). The dependence is similar to that of Ge at stress up to 120 MPa, and that of Si at stress above 120MPa. This dependence can be explained as follows under the assumption that the conduction band minimum is on near X point at zero stress. Owing to that the lowest energy of conduction band lies on near X points (<100>) up to medium stress, Si-like dependence appears. On the other hand, Ge-like dependence is shown due to that the energy level of L point (<111>) comes to be lower than that of X points (<100>) at large stress, since the energy at L points is more sensitive than that at X points on uniaxial stress along <111> direction.

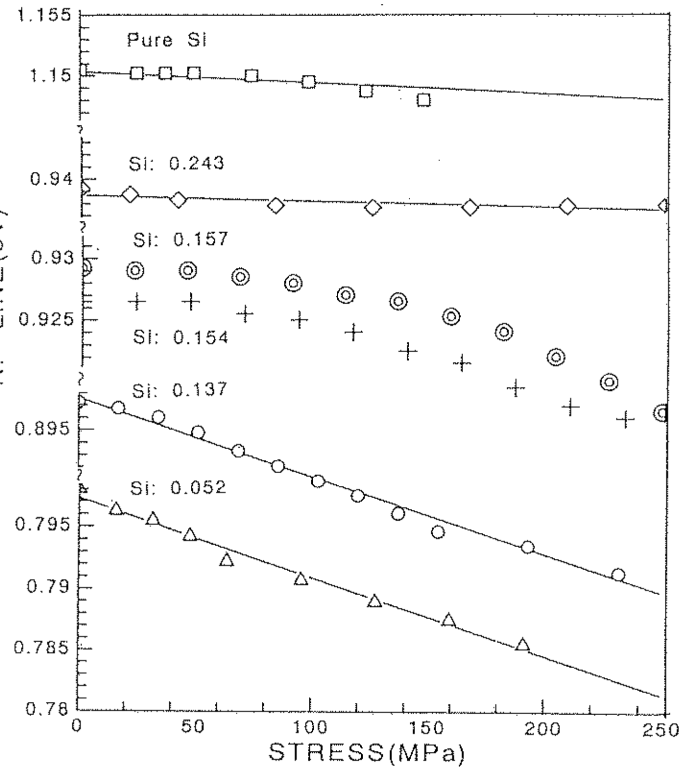
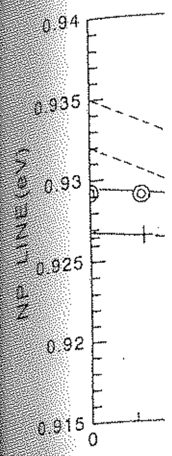


Fig. 5. The dependence of peak energy of excitonic NP line depending on uniaxial stress along <111> direction.



Conclusion

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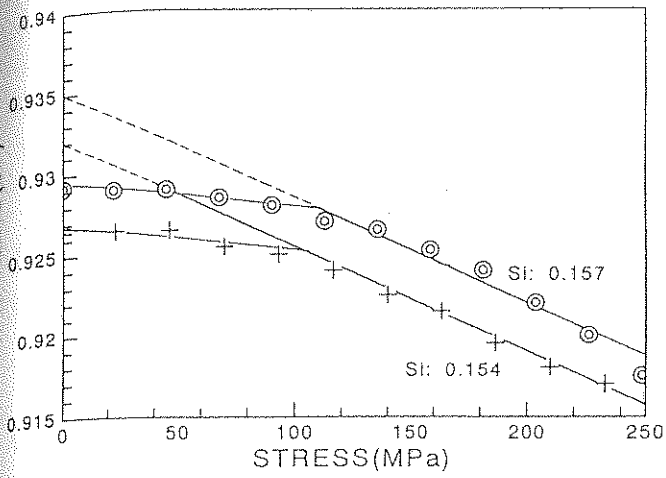

Fig. 6. The dependence of peak energy of NP line around 15 at.%Si on uniaxial stress along <111> direction.

Conclusion

The bandgap energy increases linearly in the range from 0 to about 15 at.%Si and varies gradually above 15 at.%Si. The dependence of peak energy NP line on Si composition under uniaxial stress along <111> direction changes at about 15 at.%Si, and the mixture of Ge-like with Si-like conduction band minimum is shown around 15at.%Si. From these results, it is confirmed that the conduction band minimum is on Ge-like L points (<111>) at composition up to 15 at.%Si and on Si-like X points (bottom of Δ) (<100>) above 15 at.%Si. PL spectrum related to a rising conduction band minimum under uniaxial stress along <111> direction was not detected in our experiment.

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