Efficient above-band-gap light emission in germanium

Invited Paper

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We report an above-band-gap radiative transition in the photoluminescence spectra of single crystalline Ge in the temperature range of 20−296 K. The temperature-independence of the peak position at ∼0.74 eV is remarkably different from the behavior of direct and indirect gap transitions in Ge. This transition is observed in n-type, p-type, and intrinsic single crystal Ge alike, and its intensity decreases with the increase of temperature with a small activation energy of 56 meV. Some aspects of the transition are analogous to III-V semiconductors with dilute nitrogen doping, which suggests that the origin could be related to an isoelectronic defect.

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In recent years, Ge has been demonstrated to be an excellent candidate for the fabrication of active optoelectronic devices such as photodetectors and electroabsorption modulators (EAMs) in silicon photonics[1−4]. The significant application of Ge to Si photonics is due to two major reasons. Firstly, Ge is a pseudo-direct band gap material since its 0.8-eV direct gap at the Γ valley is only 140 meV higher than the 0.66-eV indirect gap at L valleys[5]. It is this direct gap transition that enables the successful applications of Ge in photodetectors and EAMs on a Si platform. Secondly, Ge is compatible with existing Si-based nanoelectronics. In fact, SiGe materials have already been applied to high mobility complementary metal-oxide-semiconductor (CMOS) transistors[6]. Recently, our modeling has shown that Ge can also be band-engineered to behave like a direct gap material and achieve optical gain on Si[7]. While the absorption and electroabsorption properties of Ge have been extensively investigated in recent years, the light emission properties of Ge, especially the transitions above the indirect band gap of Ge, have not been thoroughly studied. Most previous reports focused on the indirect gap transition at very low temperatures of <20 K since Ge has traditionally been considered an indirect band gap semiconductor[8−10].

In this letter, we report the observation of a radiative transition, located above the indirect band gap of Ge, using photoluminescence (PL) spectroscopy on single crystalline Ge in the temperature range of 20−296 K. The temperature-independence of the peak position at 0.744±0.004 eV is distinctively different from the behavior of direct and indirect gap transitions in Ge. This transition dominates the PL spectra in the temperature range of 130−210 K, and its intensity decreases with the increase of temperature with a small activation energy of 56 meV. This peak is observed in n-type, p-type, and intrinsic bulk single crystalline Ge alike. What is remarkable about this transition is that it is above the minimum band gap (indirect gap) of Ge, which means that the associated energy levels have to be inside the conduction or valence band. This above-band-gap transition has been observed in III-V semiconductors with dilute nitrogen doping before, but it has never been reported in any group IV materials. While the origin of the transition needs further studies to identify, this observation opens a door that will lead to further understanding of radiative transitions in Ge.

A 515-nm Ar ion laser was used in the PL study. The excitation power density was ∼20 W/cm^2 for temperature-dependent PL measurements. The spectral response of the PL system has a long wavelength cut-off at 1770 nm (0.70 eV) due to the photodetector responsivity limitation. Therefore, the indirect gap PL can be observed only at temperatures lower than 150 K when the indirect gap increases beyond 0.70 eV. Different single crystalline Ge samples were used in the study, including lightly doped Ge wafers with 10^{16} cm^{-3} n-type arsenic or p-type gallium doping, intrinsic Ge bulk crystal with carrier density <10^{14} cm^{-3}, intrinsic epitaxial Ge films grown on lattice matched GaAs wafers by metal organic chemical vapor deposition (MOCVD)[11], and epitaxial Ge films directly grown on large lattice mismatch Si wafers by ultra-high vacuum chemical vapor deposition (UHVCVD)[12].

Figure 1 shows the PL spectra from the 10^{16}cm^{-3} arsenic-doped 2-inch single crystal Ge wafer in the temperature range of 22−300 K. Two peaks can be identified from the spectrum at 296 K, as indicated in Fig. 1(a). The peak at 0.793 eV corresponds very well to the direct gap transition from the Γ valley to the valence band. The other peak at 0.744 eV cannot be interpreted by the indirect transition since the indirect gap of Ge at 296 K is only 0.664 eV. Because there is no strain in the bulk Ge wafer, the peak at ∼0.74 eV cannot be explained by the strain-induced splitting in the direct gap transitions associated with the non-degeneracy of

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the light and heavy hole bands, either. However, according to the band diagram of Ge, there should be no other band-to-band transitions between the direct and indirect gap energy[5]. Therefore, the peak at 0.74 eV is an unidentified transition and we will refer to it as "peak U" in the later text. As the temperature decreases, the intensity of the direct transition peak decreases due to the fact that an increasingly smaller portion of injected carriers is distributed to the higher energy Γ valley compared with L valleys according to Fermi-Dirac distribution. The intensity of peak U, on the other hand, increases with the decrease of temperature. In the temperature range of 130−210 K, peak U dominates the Ge PL spectra and its position does not shift with temperature, as shown in Fig. 1(b). This is another feature distinctively different from the notable temperature dependence of the direct and indirect band gaps of Ge[5]. As the temperature decreases below 100 K, the indirect gap transition blue shifts to >0.7 eV and can be clearly observed in the PL spectra (Fig. 1(c)). The no-phonon (NP) transition at ∼0.73 eV and the longitudinal acoustic (LA) phonon assisted transition at ∼0.71 eV agree very well with previous reports[8]. The unidentified peak U around 0.74 eV is still present in this temperature range, and its position still remains almost unchanged. As the temperature decreases to ∼20 K, the indirect gap transition blue shifts to ∼0.74 eV and starts to overlap significantly with peak U. From Fig. 1(c), we can also see that the indirect band gap PL intensity increases much faster with the decrease of temperature than peak U. Therefore, at low temperatures of <20 K, peak U can be easily concealed by the strong indirect gap PL, which explains why this above-band-gap transition has not been observed in previous reports studying the indirect band gap emission from Ge at temperatures below 20 K.

Since peak U dominates the PL spectra in the temperature range of 130−210 K and there is almost no convolution from the direct gap or indirect gap PL in the spectra, an Arrhenius plot of peak U in this temperature range is shown in Fig. 2. The integral PL intensity of peak U decreases with the increase of temperature, and an activation energy of 56±4 meV is obtained from the plot.

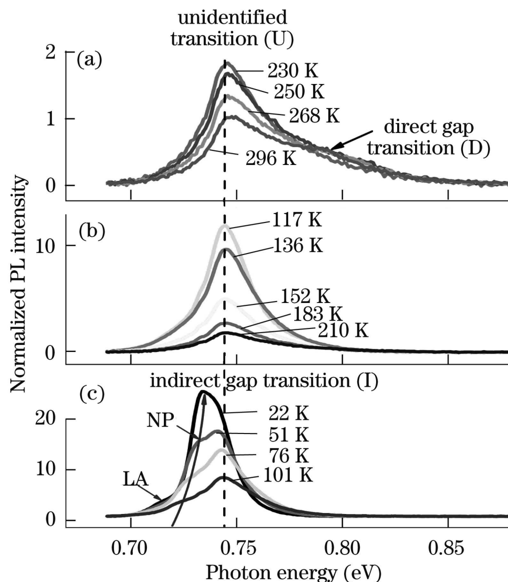

Fig. 1. PL spectra of the 10^{16} cm^{-3} arsenic doped single crystal Ge in the temperature ranges of (a) 230−296 K, (b) 117−210 K, and (c) 22−101 K.

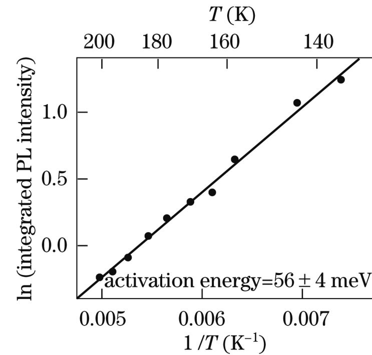

Fig. 2. Arrhenius plot of the integral intensity of peak U in the temperature range of 130−210 K. An activation energy of 56±4 meV is obtained.

Our PL study on single crystalline p-type Ge wafers (10^{16} cm^{-3} Ga doped), intrinsic bulk Ge (<10^{14} cm^{-3} dopant concentration), and high quality epitaxial Ge grown on lattice matched GaAs substrates by MOCVD with dislocation density <<10^{6} cm^{-2} also reveals the existence of peak U. However, peak U is not observed in epitaxial Ge films on 4% lattice mismatched Si substrates with a threading dislocation density of ∼10^{7} cm^{-2}, either for intrinsic or n-type epitaxial films with a phosphorous doping concentration of 10^{17}−10^{19} cm^{-3}. These results indicate that peak U exists only in very high quality Ge crystals, while the increase in defect density can quench this radiative transition.

We have also studied the behavior of peak U under tensile strain, as shown in Fig. 3. A 10^{16} cm^{-3} Ga-doped single crystal Ge sample cut from a 6-inch wafer is used, and strain is applied mechanically by bending the sample. The applied tensile strain is ∼0.05%. Both the indirect gap and direct gap transitions will red shift by a few millielectronvolts under this level of tensile strain, because the energy at the top of the valence band will increase, while the conduction band energy will decrease[13]. Figure 3 shows that peak U shifts in exactly the opposite direction from the band-to-band transition upon the application of tensile strain. This result indicates that either peak U transition

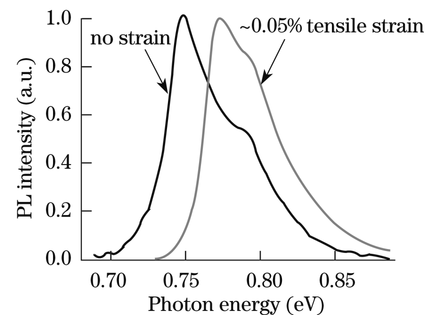

Fig. 3. PL spectra of 10^{16} cm^{-3} Ga-doped single crystal Ge under 0 and ∼0.05% tensile strain. Peak U blue shifts by ∼25 meV under 0.05% tensile strain.

does not involve the valence band or the upper energy level that contributes to the transition increases more significantly than the top of the valence band under tensile strain.

The origin of peak U is an interesting subject that needs more investigations. Clearly, it cannot be explained by any regular donor, acceptor, or mid-gap defect states since their related transition energies are all lower than the minimum band gap (indirect gap) of Ge. For example, most of the known defect states in Ge emit at photon energies close to 0.5 eV[14], which is much lower than peak U. Peak U related above-band-gap states in Ge seem analogous to the III-V materials lightly doped with nitrogen such as GaAs:N[15−17], where nitrogen forms an isoelectronic center that contributes additional states with transition energies significantly larger than the band gap. Interestingly, it has been shown that the incorporation of nitrogen can also significantly reduce the temperature dependence of direct transitions in these III-V materials, which is similar to the temperature-independent behavior of the transition related to peak U. Therefore, it seems reasonable to assume that isoelectronic centers in Ge may contribute to this above-band-gap transition. However, it has been shown that these above-band-gap levels shift in the same direction as the band-to-band transition in III-V materials upon the application of strain[17], which is opposite to what we observed for the unidentified levels in Ge. Further studies on the origin of peak U may lead to a more fundamental understanding of radiative transitions in Ge.

In conclusion, we report an unidentified above-band-gap radiative transition observed in the PL spectra of single crystal Ge in the temperature range of 20−296 K. The temperature-independence of the peak position at 0.744 ± 0.004 eV well distinguishes this transition from the direct and indirect gap transitions in Ge. The peak is observed in n-type, p-type, and intrinsic bulk single crystal Ge as well as high quality epitaxial Ge films grown on lattice matched GaAs substrates, but not observed in more defective Ge-on-Si epitaxial samples. The peak blue shifts upon the application of tensile strain, which is opposite to the behavior of band-to-band transitions in Ge. The similarity of this transition compared with nitrogen-doped III-V semiconductors suggests that this unidentified above-band-gap transition may also be related to an isoelectronic center.

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