Room temperature luminescence from Germanium

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Abstract. We analyze the band to band radiative transitions in germanium thin films deposited on silicon and compare them with those in bulk material. A significant down shift of the direct transition related peak was observed from the thin films samples, caused by the preparation formed tensile strain in the film. A comparison between the ratios of the direct to indirect transitions peak intensities showed that those are very similar for the thin films and the bulk material, when the self absorption of the emission is accounted for. The observed similarity in the spectral shape indicates that the strong direct transition luminescence detected in strained germanium films is mainly due to the improved light extraction in the energy range of about 0.8 eV, rather than an increase in the probability of band to band direct transition. We find a feature at around 0.72 eV in the spectrum of the germanium luminescence, which correlates with the presence of dislocations in the crystal. We discuss the origin of this feature in view of one dimensional dislocation bands, split off from the Gamma valley of the conduction band.

1. Introduction

Efficient light emitters compatible with standard CMOS technology have been a subject of research for more than a decade [1]. On-chip integration of light emitters would on one side significantly boost the performance of the integrated circuits by allowing fast optical data transfer, and on the other would add new functionalities to microelectronic devices for versatile optical applications [2]. A variety of concepts have been proposed [3-5], but a real application of those in process practice is still missing. Two main groups of light emitter concepts can be defined: one group embraces those which are incorporated in the silicon substrate on the so called device layer; the other covers the hybrids which in a simplistic view represent a construct consisting of direct gap materials glued onto a fully processed integrated circuit [3]. It is obvious that the compatibility requirements for the first group of devices are far more restrictive than those for the second, because they have to sustain unchanged the entire process sequence. In regard to those compatibility requirements, the material of choice for light emitters is limited to silicon, germanium and silicon-germanium alloys. Indeed, germanium has been proven as a suitable material for implementation in microelectronics and an instance of such application is the hetero-junction bipolar transistor used for high frequency digital data processing [6].

Recent reports present a new exciting application of germanium in light emitting devices. Thin, strained films grown on silicon exhibit luminescence, which maximum lies at about 0.8 eV [7-10]. It is generated by a direct transition between the conduction and the valence band. Indeed, germanium is regarded a quasi-direct semiconductor with two closely situated energy minima in the conduction

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band: a direct one at the Gamma valley and an indirect one at the L valley [11]. The energy position of the Gamma valley is just 140 mV above the L one and it can become partially filled at room temperature if the Fermi level for electrons is close to the upper band gap edge (for example in highly doped n-type materials). Partial occupation of the Gamma valley usually causes direct transition luminescence which is much more efficient than the phonon mediated indirect one, involving the L valley electrons [9].

It has been reported that at low temperatures the occupation of the Gamma valley almost vanishes due to the sharper energy distribution of the carriers. The observed intensity of the direct transition decreases with temperature corresponding to the decreasing occupation of the Gamma valley [10].

Recently it was shown that high n-type doping concentrations favor direct band luminescence, ensuring higher occupation of the Gamma valley [7, 12]. Besides doping, tensile strain in the germanium films additionally improves the probability for direct band gap transitions due to the modification of the semiconductor band structure [13]. Strain lowers the energy difference between the two minima in the conduction band and also decreases the band gap by shifting the maximum of the valence band light holes to a higher energy [14]. It has been shown that germanium becomes a direct semiconductor at strains of about 2% [15]. It is obvious that the “more direct” strained germanium films will exhibit stronger direct luminescence than the fully relaxed material.

The influence of strain and doping concentration on the efficiency of the direct luminescence has been already studied [13]. Even light amplification in thin germanium films has been reported [16]. However those studies consider changes in the luminescence in a very restricted spectral range involving only the direct band transitions related peak. Thus for example the role of luminescence self absorption in films of different thickness has been neglected. Moreover, the growth of thin germanium films on silicon substrates is related with formation of crystal defects, which also exhibit luminescence in the energy range 0.45-0.58 eV [17, 18]. Although there is no doubt that the reported luminescence enhancement effects are primarily due to the doping and strain of the germanium layers, the role of their material quality and its influence on the luminescence properties has not yet been clarified sufficiently.

Here we report on the luminescence of undoped and differently doped p- and n- type bulk germanium samples and make a comparison with the luminescence obtained from non-doped thin germanium films prepared by chemical vapor deposition (CVD) on silicon substrates [19]. For a bulk reference sample containing dislocations we used a wafer from a poly-crystalline block cast grown crystal. The reported spectra are recorded over a broad spectral range, so that indirect band to band transitions as well as defect related luminescence can be analyzed. We consider the role of the self absorption of the direct luminescence in bulk germanium and discuss the stricture of the indirect band transition peak. Moreover, spectral features in the low energy range are detected and identified as dislocation related peaks. We confirm the correlation between the appearance of those features and modification in the fine structure of the indirect band to band transition luminescence, which was already reported in the work of Kittler et al [19].

2. Experimental Method

2.1. Samples

Eight wafers of Czochralski <100> grown (Cz) bulk germanium were investigated. Four of them were n-type doped by Sb and the other four were p-type doped by Ga. Doping concentration in each case was varied from $10^{15}$ to $10^{16}$ cm$^{-3}$. In addition, undoped germanium wafers and undoped thin germanium layer samples were studied. The thin germanium films were prepared by CVD of germanium on a silicon substrate. The dislocation density for the CVD samples was estimated to be $10^7$ cm$^{-2}$. The germanium layer was 5 µm thick and was not intentionally doped. To understand the influence of the dislocations on the luminescence from the thin films we examined the luminescence from wafers of poly-crystalline block-cast-grown-germanium and compared its spectrum with that of the thin film sample. Details of the poly-crystalline samples can be found in [20].
2.2. Setup for luminescence measurements
For the PL study reported below we used a standard spectroscopic setup. The Germanium samples were excited by means of a frequency doubled Nd:YAG diode-pumped solid-state laser, emitting continuous-wave at wavelength of 532 nm. The spot of the laser beam at the surface of the sample was about 100 µm in diameter. The laser power used for excitation was in the range of 100 mW to 2 W. The luminescence was collected by a parabolic mirror and spectrally analyzed by a monochromator (0.64 m focal length, F/5.2 aperture) equipped with a 300 l/mm grating and an InSb detector. The excitation beam was chopped at 133 Hz and a lock-in technique was used to process the signals.

3. Results and discussion
The luminescence from the bulk samples shows two distinct peaks with maxima at about 0.7 and 0.8 eV. Examples of the as-measured spectra on samples with different doping type but similar doping concentration are shown in figure 1.

![Figure 1](image.png)

**Figure 1.** Luminescence from bulk Germanium samples.
(A) Spectra measured on p and n type doped samples with similar doping concentrations ($10^{15}$ cm$^{-3}$).
(B) Dependence of the direct band transition peak intensity on the doping concentration.

The maximum of the intensity of those spectra appears in the energy range of the indirect band to band transition. The shape of the spectra for both doping types is alike and no indication for a stronger luminescence from the Sb doped n-type samples was found. Surprisingly, the luminescence from the p-type Ga doped samples appears even stronger than that for Sb doped ones at concentration of about $10^{16}$ cm$^{-3}$. Indeed, the doping concentration used here is small, and one cannot expect that the position of the quasi Fermi levels at high excitation would significantly be influenced by it, but the results imply that the luminescence intensity is also influenced by factors related to the quality of the material, especially when the doping concentration is low. We should mention that detectable direct band recombination is recorded in low n-doped and even p-doped samples so a high n-doping is not necessarily the reason for its appearing.

All measurements presented in figure 1 are carried out at equal excitation conditions and the intensity ratio of the radiation due to direct and indirect related transition, from all samples is same. Upon increasing the excitation the direct band transition related peak increases. Figure 2 shows spectra recorded at different power of the excitation beam from a non-intentionally doped sample. The curves are normalized to the maximum of the indirect transition peak.
Figure 2 shows the dependence of the direct, $I_d$, and indirect, $I_i$, transitions intensities on the excitation power $P$. Both data sets can be well described by a power law $I \sim P^n$, where $n=1.4$ for the indirect and $n=2.1$ for the direct transition. Considering that the material is non-doped, the intensity of the luminescence should be proportional to the square of the injected carriers, because each emitted photon is generated from a recombination of a pair of excess electron and hole. The recombination rate is then proportional to the product of the concentrations of electrons and holes and each of those is proportional to the excitation power \cite{21, 22}.

![Figure 2. Intensity of direct and indirect recombination peaks dependence on the excitation level. (A) Spectra normalized on maximum, taken at different powers of the excitation laser beam. (B) Log-log plot for estimating excitation dependence of the direct and indirect radiative transition peaks.](image)

The near quadratic dependence observed for the direct transition luminescence matches well the expected one, but there is no such match in the case of indirect band luminescence. A possible reason for the sub-quadratic dependence of the indirect band luminescence is a competitive process of non-radiative recombination, which effectively restricts the increase of electron concentration in the L valley of the conduction band upon increasing excitation power. A candidate for such a competitor is the Auger recombination. Indeed, the concentration of the electrons in the L valley is significantly higher than that in the Gamma valley and the probability of a three carrier mediated Auger process with energy transferred to a second electron should also be relatively high. One can assume that the Auger recombination ($Cn^3$) is limiting the concentration of electrons, $n$, in the L valley. The generation rate ($\sim$ excitation power), $G$, is equilibrated by the Auger recombination ($G=\text{C}n^3$), so that the concentration of carriers $n$ in the L valley should be proportional to the excitation to the power of 1/3.

The indirect radiative recombination rate is then given by the product of the electron density in the L valley ($\sim P^{1/3}$) and the hole density in the valence band ($\sim P$). This leads to an indirect transition rate proportional to the power of 1.3, which is close to the experimentally obtained result.

We use the above quadratic dependence of the direct recombination on the excitation to derive the correction for the luminescence-self-absorption in bulk germanium. The spectra shown above represent the wavelength dependent intensity distribution of the luminescence which escaped from the sample after passing through a significant amount of material. To obtain the truly generated luminescence spectrum one should account for the self-absorption in germanium itself. Indeed, the intensity of the indirect radiation is barely influenced, while a significant part of the direct radiation is absorbed. To correct the spectra for self absorption we assumed that the luminescence intensity is proportional to the square of the generated excess carriers.
In the case of photo-excitation with a green laser (532 nm) the light is absorbed in a few nm beneath the surface and the carriers generated there diffuse into the bulk. Their density exponentially decreases in depth with a scaling factor corresponding to their diffusion length.

Similarly the luminescence \( I(h\nu) \) generated at a certain depth passes a layer with absorption coefficient \( \alpha(h\nu) \) and is attenuated exponentially.

Assuming one dimensional distribution and integrating all contributions from recombinations at different depths we obtained a relation for correcting the spectra due to the self absorption:

\[
I_{\text{meas}}(h\nu) = I(h\nu) \cdot \left( e^{-\alpha(h\nu)} + \frac{1}{L_d} \right)^{-1}.
\]  

(1)

In the equation above \( I_{\text{meas}}(h\nu) \) denotes the luminescence intensity escaped from the sample, \( I(h\nu) \) denotes the intensity of the generated luminescence, \( \alpha(h\nu) \) is the absorption coefficient, and \( L_d \) stands for the diffusion length of the excess carriers. In all parameters the term \( h\nu \) marks their photon energy dependence.

To obtain the spectra corrected for self absorption we measured the spectrum of the absorption coefficient of the samples, utilizing the same spectrometer and detector, which we used for luminescence measurements. The data were normalized to fit those available in the literature \[23, 24\]. The diffusion length was taken to be 100 µm, a typical value for the investigated material.

Figure 3 shows a spectrum of an Sb doped sample with correction for the self absorption. A non corrected spectrum is added for comparison. It is seen that the intensity of the direct transition exceeds the indirect one about 10 times. A similar value has been reported in an earlier study \[25\]. Moreover, the position of the direct transition related peak in the corrected spectrum is at 0.8 eV, exactly corresponding to the reported value for the direct band gap energy.

The diagrams in figure 3b present a fit of the corrected spectra with the known dependences for direct and indirect allowed transitions in a semiconductor.

The peak shapes according Bebb and Williams \[26\] are given by:

\[
I_d(h\nu) \sim \frac{E_g}{E_g - h\nu} \cdot \exp\left(\frac{E_g - h\nu}{kT}\right)
\]  

(2)

for a direct transition and

\[
I_i(h\nu) \sim (E_g - h\nu)^2 \cdot \exp\left(\frac{E_g - h\nu}{kT}\right)
\]  

(3)

Figure 3. Spectra of band to band transition of an Sb doped sample normalized on maximum. (A) Corrected for self-absorption. (B) Fit of the spectral features in the indirect transition peak. The inset shows the fit of the whole spectrum with the indirect- and direct-transition related peaks.
for the indirect one. Here \( I_d(hv) \) and \( I_i(hv) \) denote the intensity of the luminescence due to direct and indirect transitions, \( E_{gd} \) and \( E_{gi} \) are the direct and the indirect band gaps, \( kT \) is the mean thermal energy term at room temperature, and \( hv \) is the energy of the emitted photons.

For the indirect related feature three peaks of similar intensity were used to fit its fine structure. The difference in the position of those peaks is 28 meV, which corresponds to the energy of the longitudinal acoustic phonons in germanium at the L point [27]. Those peaks we relate to phonon mediated radiative recombinations, namely, one phonon emission, one phonon absorption, and zero phonon transitions.

To estimate the real enhancement of the direct luminescence in germanium thin films we use the intensity of the indirect transition as a reference. Figure 4 compares the spectra of a thin germanium sample with that of the bulk one, but corrected for the self-absorption. A correction for the thin sample spectra is not necessary, because of the negligible attenuation of the luminescence inside the thin film.

**Figure 4.** (A) Band to band luminescence spectra from thin strained samples compared with that from bulk material. (B) Band to band luminescence feature in the spectrum of a poly-crystalline germanium sample containing dislocations.

Figure 4A shows that the luminescence spectra from the thin film sample and the corrected bulk samples are similar. The spectrum from the thin film sample shows a well pronounced shift of the direct transition related feature, which we consider caused by the strain induced band gap shrinkage. The strain originates from the thermal expansion coefficient mismatch between the germanium film and the silicon substrate. The germanium is deposited on the substrate at a temperature of about 800°C. By cooling down to room temperature it undergoes a stronger contraction than silicon and the thin film becomes tensile strained.

It can be seen that the ratio between direct and indirect transitions features in both spectra is similar. Considering the enhancement of the direct luminescence in the thin strained films, one can state that the major effect is due to the better light extraction from the film. In fact we do not observe any improvement of the direct transition related luminescence due to the strain, because the ratio between direct and indirect transition peaks is similar to those for the bulk sample (when corrected for the self-absorption).

But let us consider the spectra in more detail. A peak at 0.72 eV is observed in the spectrum of the thin film sample, which is not present in the spectrum of the bulk material. A similar peak is also detected in the poly-crystalline samples containing dislocations (figure 4B). We relate that peak with the presence of dislocations in the crystalline lattice. Indeed, well known dislocation related features are observed in the luminescence spectra of plastically deformed germanium samples in the range 0.45-0.58 eV [28]. Figure 5 shows the spectra of epitaxially grown thin germanium films recorded at
room temperature and at 80 K exhibiting the above mentioned dislocation spectral features. Similar spectra were recorded on the poly-crystalline samples as well.

![Graph of PL vs Energy](image)

**Figure 5.** Dislocation related features in the spectrum of a 5 µm thin germanium layer on silicon.

The presence of a peak at around 0.72 eV in the spectra of samples with dislocations and its absence in the high crystal quality Cz samples suggests that it originates from extended defects. The origin of the dislocation radiation is still not fully understood and is a subject of intensive research [29]. However, some of the characteristic features can be related to formation of one dimensional dislocation bands due to the modification of the semiconductor three dimensional energy bands by the local dislocation strain field. A general expression for such modification is given by Lelikov et al [30].

\[
E_{\text{dis}} = E_g - A \left( \frac{\alpha}{\alpha_g} \right)^2
\]

where \( E_{\text{dis}} \) is the energy of the radiation, \( E_g \) is the band gap, \( \alpha \) is the lattice constant, \( A \) is a constant accounting for the deformation potential and the effective mass of the carriers, and \( b \) is the edge component of the Burgers vector of the dislocation.

A modification of the direct as well as the indirect band gaps could be expected. We think that the observed feature at around 0.72 eV is a result of the dislocation related direct gap modification of germanium. A shift of the dislocation related bands of about 80 meV below the direct band edge is expected by an evaluation of the material specific parameters [31].

4. **Conclusions**

In this work we analyzed the band to band luminescence of germanium bulk material and compared with that from thin germanium films deposited on silicon. Spectral features in the region of direct and indirect transitions were discussed. A strong direct transition luminescence peak was found in the spectra from the thin film germanium samples. The peak was slightly downshifted from its expected position at 0.8 eV, indicating tensile strain in the film. A comparison of the spectra from the bulk and from the thin film germanium samples, excluding the role of self absorption, showed that both are very similar in shape. This observation let us to conclude that the main reason for the observed strong luminescence from the thin films is the improved light extraction of the direct transition radiation.

We showed that the samples containing dislocations have an additional peak at about 0.72 eV in their spectrum, which is not present in the spectrum of the defect free germanium crystals. We related this peak to the dislocations and their long range strain field. We suggested that the dislocation induced strain modifies the direct band gap of germanium locally, forming a one dimensional band along the dislocation line, shifted by about 80 meV below the direct band of the bulk material.
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