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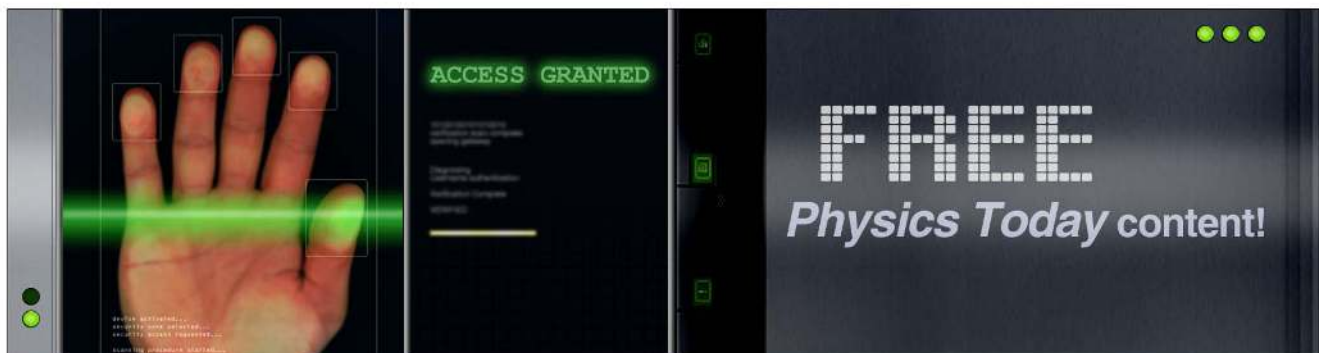
Direct band gap narrowing in highly doped Ge

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Direct band gap narrowing in highly doped n-type Ge is observed through photoluminescence measurements by determining the spectrum peak shift. A linear relationship between the direct band gap emission and carrier concentration is observed. We propose a first order phenomenological model for band gap narrowing based on two parameters whose values for Ge are $E_{BGN} = 0.013\,eV$ and $\Delta_{BGN} = 10^{-21}\,eV/cm^{-3}$. The application of these results to non-invasive determination of the active carrier concentration in submicron areas in n-type Ge structures is demonstrated. © 2013 AIP Publishing LLC [http://dx.doi.org/10.1063/1.4802199]

Tensile strained n^+ doped Ge shows promise as a light emitting material for fully integrated silicon photonic applications. The combination of modest tensile strain and n-type doping makes epitaxial Ge-on-Si a pseudo-direct band gap emitter, but the emission efficiency for electrically pumped devices is projected to be practical only if doping levels greater than $10^{19}\,cm^{-3}$ can be achieved.[1–3] Furthermore, the incorporation of dopants must not introduce point defects into the Ge crystal structure, since these can significantly reduce emission efficiency.[4] Unfortunately, implantation techniques, which can raise the dopant concentration, generally introduce defects. Therefore, the total dopant concentration from implantation does not equal the total *active* dopant concentration.[1,5,6]

The most common process for determining dopant concentrations is secondary ion mass spectroscopy (SIMS). However, SIMS is disadvantageous because active dopant concentrations cannot be determined. Furthermore, this technique is destructive as material is removed during the measurement. Other techniques such as Hall Effect measurement, which can determine an average concentration of dopants, are limited by the sample size needed. We propose in this paper a technique using photoluminescence (PL) to determine average active doping based on band gap narrowing (BGN).

A shift in absorbed or emitted wavelength due to doping is known as BGN and has been observed in many semiconductor materials. BGN has also been observed in unstrained Ge through infrared absorption measurements.[7] Tensile stressed Ge-on-Si has been known to emit at $\sim$1550 nm at dopant concentration up to $1 \times 10^{19}\,cm^{-3}$ with insignificant changes in the peak emission wavelength.[1,2,8] Under degenerate doping, $n > 1 \times 10^{19}\,cm^{-3}$, a clear shift in emission wavelength is observed.[9]

The most recent BGN model presented by Jain *et al.*[6,10] shows bandgap shrinkage due to carrier concentration in the L valley and temperatures <77 K. The expression for Ge in Jain's paper does not include strain, which also narrows the band gap, hence, shifting the PL emission peak. Furthermore, Jain's model fails to address band gap emission shifts due to high doping level at high temperatures as well as direct band gap shift.

Here, we present a study on BGN at 300 K for phosphorus concentrations of $5 \times 10^{18}\,cm^{-3}$ to $4.5 \times 10^{19}\,cm^{-3}$ in Ge. Our experimental results confirm that Jain's BGN theory[6] is only appropriate for low temperatures (<77 K) and for the indirect L band gap in Ge.

Germanium films were grown epitaxially on bulk silicon substrates with (100) orientation by ultra-high vacuum chemical vapor deposition (UHVCVD). Details of the deposition process have been described previously.[1,11,12] Ge films were deposited in a two-step process, beginning with a low-temperature deposition of a thin but highly defective Ge buffer epitaxial layer. This buffer layer relaxes the strain induced by lattice mismatch of 4.2% between Si and Ge at the substrate interface and serves as a sink for dislocations. On top of the buffer layer, a high-temperature co-deposition of Ge and P creates a thick layer of high quality crystalline n^+ Ge with a carrier concentration of $1 \times 10^{19}\,cm^{-3}$. Then, delta doped Ge layers are deposited. They consist of monolayers of P encapsulated by intrinsic Ge.[11] The upper cladding of the material is provided by a PECVD SiO_2 layer. P is diffused into the n^+ Ge film by rapid thermal anneal (RTA). The oxide layer acts as a diffusion barrier. Details of the P diffusion can be found in Cai *et al.*[12] The Ge threading dislocation density is $\sim$3 $\times 10^8\,cm^{-2}$ in the delta doped region and $\sim$10$^7\,cm^{-2}$ in the intrinsic doped Ge from TEM measurements. The point defect density is assumed to be $\sim$10$^7\,cm^{-3}$ from the law of mass action.

Blanket films and waveguides were fabricated and then measured using x-ray diffraction (XRD) and PL. The different dopant concentrations were analyzed using SIMS, Hall Effect, and PL measurements. A Horiba MicroPL system utilizing a 1064 nm laser with a maximum power density of $\sim$0.05 mW/μm^2, and an EOS InGaAs IGA1.9 photodetector were used at room temperature (RT) to measure the photoluminescence spectra of the Ge samples. The detector cutoff is at $\sim$2100 nm at RT. The samples were measured with a temperature control stage to eliminate extraneous effects such as lattice temperature increase.

Samples with P concentrations ranging from 5×10^{18} to $4.5 \times 10^{19}\,cm^{-3}$ were studied. XRD measurements showed that both blanket films and waveguides have similar tensile strain of $\sim$0.25%.

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It has been shown that an increase in PL intensity in Ge is equivalent to higher active carrier concentrations in Ge when retaining low defect concentration.[6,13] SIMS and Hall effect measurements confirm that the dopants in Ge are fully activated, hence, they can be treated as free carriers capable of contributing to the direct band-gap emission. As expected, the total integrated PL emission also increases, indicating insignificant defect related traps, and confirming that active dopants are contributing to emission. In addition to such increase of PL intensity, we also observe a redshift of the peak wavelength for the direct band gap emission with higher doping concentration, as seen in Figure 1. The PL emission originates from the band-edge of the direct Γ valley.[1] Hence, the PL peak emission is equivalent to the energy gap, E_Γ, in agreement with the previous calculations and experiments.[1] The wavelength shift indicates BGN of the Ge Γ-valley transition. Although change of strain may also result in a shift of the bandgap, cross-analysis with XRD shows that even at these high doping levels, dopant concentration used in these experiments are not sufficient to relax the lattice strain. We therefore consider a model only based on carrier interactions to explain such BGN effects. BGN also provides a simple, non-destructive measurement technique to determine doping concentrations of samples smaller than permitted for standard methods. Since the Fermi level is still below the Γ-valley, Boltzmann distribution is used to interpret the emission spectrum. The energy of the peak emission is kT/2 higher than the direct bandgap. k is the Boltzmann factor and T is the temperature. The band gap without BGN is calculated by adding kT/2 to the energy difference between valence band maximum and Γ-valley minimum. The difference between the PL peak emission for doped and undoped Ge provides the BGN in the Γ-valley.

Haas presented his observation of direct BGN of Ge by analyzing the absorption spectrum.[10] This method takes into account recombination of carriers from valence band to L-valley band edge. Both absorption and emission mechanisms show equivalent results for Γ-valley at 300 K, as shown in

Figure 2. Our data fit Hass's 300 K data[13] and suggest a lower limit for BGN, as will be discussed. The extensive experiments in this work show a linear dependence of Γ-point band gap shrinkage with heavy n-doping.

From first principles, theoretical treatment of the experiments in this work may need to consider two distinguishing features: (i) the experiments were performed at 300 K, and (ii) Ge is tensile strained moving L- and Γ-band minima closer together.

This approach might be generalized for Ge according to the following equation:

$$E_g(N_D = 0) - E_g = E_{BGN} + \Delta_{BGN}N_D(\text{cm}^{-3}), \qquad (1)$$

where N_D is the dopant concentration, E_{BGN} is BGN turn-on offset energy reduction (intercept of the linear relationship at $N_D = 0$); and Δ_{BGN} is the BGN coupling parameter (slope of the linear dependence of E_g reduction with N_D). The data of this work yield the following parameters: $E_{BGN} = 0.013$ eV and $\Delta_{BGN} = 10^{-21}$ eV/cm^{-3}.

We propose that the linear dependence can be regarded as the dominant first order term of a BGN phenomenological model. The linear fit, therefore, can be used to predict with reasonable accuracy the spontaneous emission wavelength of doped Ge and to measure through such emission the doping level of the Ge.

This functional dependence contrasts with predictions of the Jain model[6] for the L-valleys and of the simplified lower-limit model further discussed in this work. However, the experimental values of all observations fall between the predictions of the two models.

Jain's model for BGN assumes a static lattice model for temperatures <77 K. It has four components[6]

$$\Delta E_g = \Delta E_x + \Delta E_{cor(min)} + (\Delta E_{i(maj)} + \Delta E_{i(min)}). \qquad (2)$$

In n-type semiconductors, the exchange interaction, ΔE_x, is defined by the electron interactions in the different sub-bands, which is described by Hartree-Fock potentials.[14] The shift of the holes is considered in the electron-hole correlation energy, $\Delta E_{cor(min)}$; and the shift of electrons (*maj*)
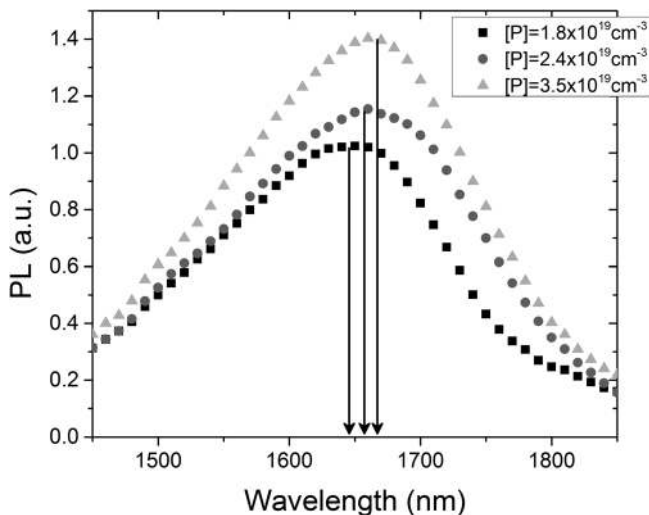

FIG. 1. PL intensity for heavily n-type doped Ge. BGN shift in emission compares to doping concentration of samples analyzed. Arrows show peak shift from the different doping concentrations, red shifting with increasing active dopant.
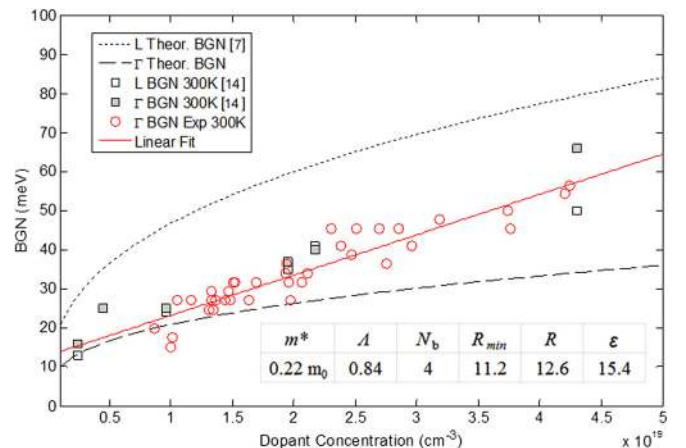

FIG. 2. Experimental observations of BGN as a function of n-type doping concentrations at 300 K. A linear relationship is observed. The data fall between Jain's theory (L-band) and Eq. (4) of this work for the minimum change (Γ-band).The insetted table shows parameters used in Eqs. (3) and (4).

and holes (*min*) due to carrier impurity interactions is represented by $\Delta E_{imp} = \Delta E_{i(maj)} + \Delta E_{i(min)}$. If the shift of the L valley is considered, the equation has the following form:[6]

$$\frac{\Delta E_g}{R} = 1.83 \frac{\Lambda}{N_b^{1/3}} \frac{\delta}{r_s} + \frac{0.95}{r_s^{3/4}} + \left[\delta + \frac{R_{(min)}}{R}\right] \frac{1.57}{N_b r_s^{3/2}}, \quad (3)$$

where N_b is the number of interacting sub-bands, Λ is the correction factor due to anisotropy in the conduction band, R is the effective Rydberg energy for both majority (R) and minority carriers (R_{min}), and r_s is an dimensionless unit from the half average distance between impurities, r_a, under the effective Bohr radius, a.

In the classic low-temperature model, inter-valley interaction is limited and electrons can only have exchange and scattering effects within their own sub-valley. Such effect in the L valleys is much larger than that for the Γ valley, reducing ΔE_x and $\Delta E_{i(maj)}$ for the Γ-valley. Thus, for the Γ-valley, only the correlation energy $\Delta E_{cor(min)}$ and the impurities interaction of valence band $\Delta E_{i(min)}$ are left in the equation. Since $\Delta E_{cor(min)}$ and $\Delta E_{i(min)}$ reflect only changes on the energy of states in the valence band, the same values can be used for L and Γ valleys. The equation becomes

$$\Delta E_\Gamma = 8.15 \left(\frac{N}{10^{18}}\right)^{1/4} + 2.03 \left(\frac{N}{10^{18}}\right)^{1/2}. \quad (4)$$

This equation expresses the unique contribution of carrier concentration to the band gap shrinkage at the Γ point in Ge. This expression should be regarded as the minimum band gap shrinkage because carrier redistribution due to higher temperatures will further reduced the band gap. As seen in Figure 2, the ΔE_Γ prediction is undervalued at 300 K.

At 300 K, an increase of doping concentration clearly narrows the band gap, and the energy reduction follows a linear relationship with doping. It is significant to observe that Hass's data[10] for both L and Γ BGN, and our data follow the same linear relationship at 300 K, as seen from Figure 2. In this context, the similar BGN effects observed by Hass for the Γ-point and L-points conflict with Pankove's modified k-space theory.[15] One possible reason is that more electrons will go into the Γ valley at high doping and that temperature may generate a larger exchange interaction, ΔE_x. Another possible reason is the effect of impurity band formation at high doping. An impurity band would enhance the interaction between electrons in L and Γ-valleys, weaken momentum conservation, and may average the energy shift in different valleys. Thermal energy can also increase interaction between Γ and L valleys by providing energy for inter-valley scattering transitions.[16]

From our PL results, the peak emission shift reflects the free carrier concentration and, since all dopants are activated, the dopants concentration. By using Eq. (1), we can determine the active dopant concentration by analysis of the PL spectrum, and vice versa. Within the tensile strain values studied in our Ge films of 0%-0.3%, we find no evidence that doping induced BGN is modified by strain.

This work shows that BGN measured from a PL spectrum can be used as a nondestructive technique to determine active carrier concentrations in heavily doped Ge. This technique could be extended to other semiconductors with similar behavior.

In summary, we measure significant red-shifts in the photoluminescence spectra of degenerately n-doped, tensile strained Ge. The red-shift exhibits a linear dependence on doping level that we have interpreted as BGN. We propose a first order phenomenological model for BGN based two parameters whose values for Ge are $E_{BGN} = 0.013$ eV and $\Delta_{BGN} = 10^{-21}$ eV/cm^{-3}. BGN can be a powerful nondestructive method for determining the total active dopant concentration in Ge-on-Si devices.

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