Substitutional gold in $Si_{1-x}Ge_x$

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It is demonstrated that relaxed $Si_{1-x}Ge_x$ of $0 \leqslant x \leqslant 0.25$ grown by molecular beam epitaxy, using the compositional grading technique, can be doped with gold by a high-temperature indiffusion process from a deposited gold layer. Substitutional gold in both *p*- and *n*-type alloy layers has been identified and characterized by deep level transient spectroscopy, and the donor and acceptor levels of neutral, substitutional gold in the SiGe alloys were studied as a function of the Ge content. The data suggest that both the donor and acceptor levels are pinned to the conduction band. [S0003-6951(96)00538-4]

It is now generally accepted that the donor and acceptor states of Au in Si at $E_V+0.34$ eV and $E_C-0.55$ eV, respectively, both originate from isolated, substitutional gold in the neutral state.[1] Very few investigations on deep level states in germanium have been reported in the literature[2] and, to the knowledge of the authors, there has been no report on deep levels related to gold in germanium. Hellqvist *et al.*[3] and Kissinger and Grimmeiss[4] have studied Au-doped SiGe alloys by photothermal ionization spectroscopy and absorption measurements. From the absence of any line spectra in their measurements, except in one case, they concluded that the Au impurities precipitated at extended defects, and that the concentration of isolated Au impurities therefore decreased considerably.

In this letter, we demonstrate by deep level transient spectroscopy (DLTS) measurements the feasibility of incorporating Au in relaxed $Si_{1-x}Ge_x$ alloy layers for $0 \leqslant x \leqslant 0.25$, grown by molecular beam epitaxy (MBE), by a post-growth indiffusion process from a deposited Au layer.

Relaxed $Si_{1-x}Ge_x$ layers of $x=0.05$, 0.15, and 0.25 were grown by MBE on (100) Si substrates using the compositional grading techniques as described previously.[5] Both p^+-n and n^+-p diodes were fabricated by first growing a 4 μm thick layer doped with $2-5\times10^{15}$ cm^{-3} of, respectively, antimony or boron; on top of this layer, a 0.5 μm thick layer doped to a very high concentration of, respectively, boron or antimony ($\sim1\times10^{19}$ cm^{-3}) was grown. Mesa diodes were formed by chemical etching of photolithography-defined areas. Pure Si diodes were fabricated by epitaxial growth of thin layers (2000 Å) doped with B or Sb on top of commercially available Si substrates doped with P or B, respectively. A pure Si *n*-type layer, doped with Sb, was also grown by the MBE technique described above.

Gold was diffused into the mesa diodes from thin ($\sim$0.1 μm) aligned gold layers deposited on top of the mesa diodes; different diffusion temperatures between 600 and 800 °C were used with a diffusion time of 24 h. No deep levels of intensities corresponding to concentrations higher than 5×10^{12} cm^{-3} were observed in the diodes before the gold indiffusion step. Blind diodes, without deposited gold layers, were also processed at high temperatures; there was no indication of any process-induced levels in the DLTS spectra. The DLTS spectra were measured using a commercial Semitrap spectrometer.

For all the investigated compositions, and for the same conduction type, qualitatively similar spectra were obtained. In the *n*-type materials (p^+-n diodes), spectra consisting of only one dominating line were measured (Fig. 1); this line is assigned to the acceptor level of substitutional gold in the SiGe alloys from the knowledge of gold in silicon.

In the *p*-type materials (n^+-p diodes), the spectra consist of two lines, which is also in agreement with the findings in silicon (Fig. 2); these lines are assigned to the donor level of substitutional gold (the line at 110–170 K) and to the acceptor level (the line at 240–290 K) which also appears in the *p*-type materials due to a population change.[6] In the spectra shown in Fig. 2 there are two effects which would catch the eye, first, that all the lines move towards lower temperatures with increasing Ge content, and second, that the intensity of the line correlated to the acceptor level in the *p*-type materials increases with increasing Ge content up to $x=0.15$ and then saturates. This effect was studied as a function of injection-pulse length and the shown spectra are all recorded with an injection pulse sufficiently long to ensure complete saturation of both traps.

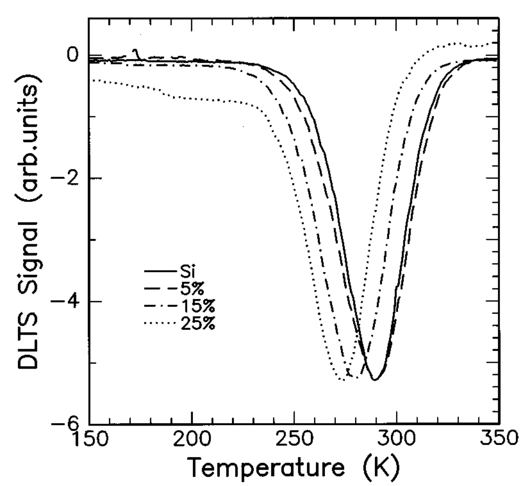

FIG. 1. DLTS spectra from Au-diffused p^+-n SiGe samples; the indiffusion was done at 800 °C for 24 h. The 5%, 15%, and 25% spectra have been normalized to that of pure Si; a repetition rate of 5 ms was used.

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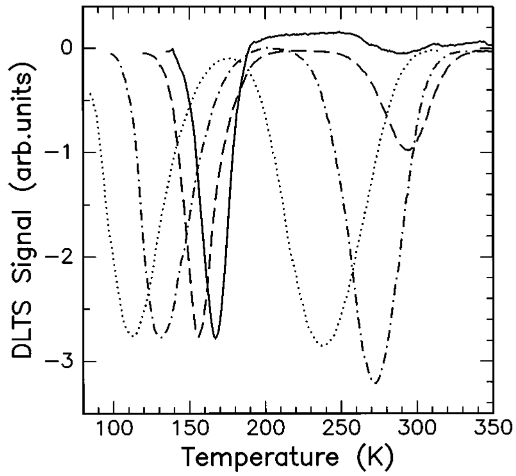

FIG. 2. DLTS spectra from Au-diffused n^+-p SiGe samples; the indiffusion was done at 800 °C for 24 h. The 5%, 15%, and 25% spectra have been normalized to that of pure Si

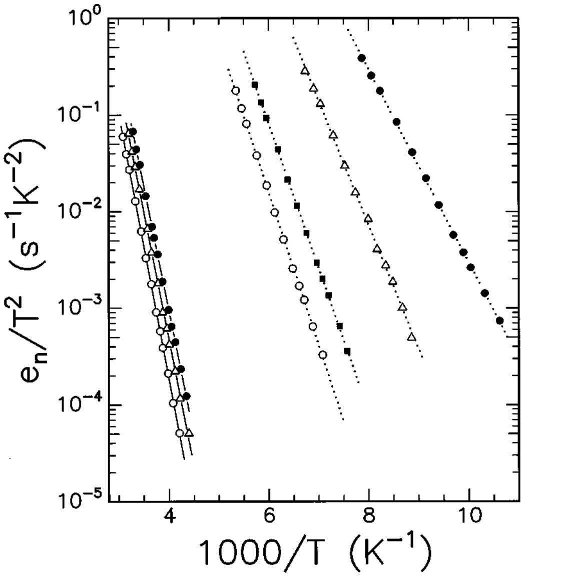

FIG. 3. Arrhenius plots of the Au acceptor level (electron trap) measured in n^+-p samples (solid line) and the donor level (hole trap) measured in n^+-p samples (dotted line). (○) pure Si, (■) 5% Ge not shown for the n^+-p sample, (△) 15% Ge, and (●) 25% Ge.

The measured activation enthalpy and apparent capture cross section for the peak in pure Si (Fig. 1) are in agreement with the accepted values for the acceptor level of substitutional Au in Si.[1] Likewise, the values for the activation enthalpies and apparent cross sections for the peaks in pure Si in Fig. 2 are in agreement with the values for the donor and the acceptor level of Au. In addition, as-grown diodes heated without deposited Au showed no peaks other than those present after growth; based on these observations, we ascribed the observed peaks in SiGe to the donor and acceptor level of substitutional Au in SiGe.

Depth profiling of the traps was also performed utilizing the double pulse technique. A slightly decreasing profile towards the bulk was found, in agreement with Au indiffusion from the surface.

The Au concentrations corresponding to the acceptor signals in Fig. 1 and the donor signals in Fig. 2 are between 3×10^{13} and 3×10^{14} cm^{-3}. These concentrations are lower than the solubility values listed in the literature[7] for gold in silicon; this phenomenon could be linked to surface and/or interface states, but we are currently investigating the Au-equilibrium concentration as a function of both temperature and Ge content.

Arrhenius plots for the different lines and compositions constructed from temperature scans performed at different pulse frequencies are shown in Fig. 3; the Arrhenius plot for the Au acceptor in $x=0.05$, p^+-n sample has been omitted for clarity reasons. From the slopes and intercepts of the Arrhenius plots, the DLTS finger prints of the deep levels have been extracted, namely the activation enthalpy and the apparent capture cross section; these parameters are presented in Fig. 4. No measurable difference between diodes formed on MBE-Si doped with Sb and P-doped Si was observed.

Preliminary measurements of the absolute capture cross section as a function of Ge concentration together with the apparent capture cross sections as given in Fig. 4(b) indicate that the entropy of ionization for both the acceptor and the donor states is initially small and almost independent of the Ge concentration. Hence, entropy variations can be excluded as a major cause of the activation enthalpy changes versus Ge concentration, as demonstrated in Fig. 4(a).

Apart from a small increase in the activation enthalpy in going from $x=0.0$ to $x=0.5$ for the acceptor level measured in n-type material, the activation enthalpy for this level decreases slightly from $E_c-0.547$ eV for $x=0.0$ to E_c

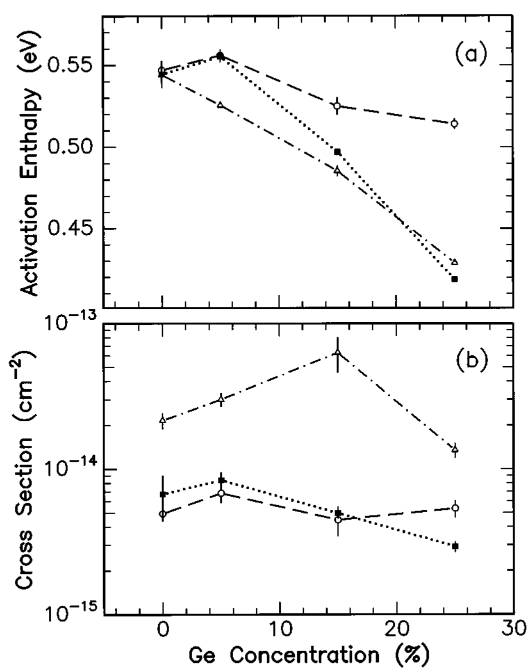

FIG. 4. Extracted activation enthalpies and capture cross sections shown as a function of Ge content. (○) acceptor level (electron trap), (■) acceptor level (hole trap), and (△) donor level. The donor values have been shifted 0.23 eV. The error bars indicated are one set of sigma values obtained from the fitting procedure.

-0.514 eV for $x=0.25$. For the acceptor level, in the p-type material, a similar small increase is found in going from $x=0.0$ to $x=0.05$; the reduction in the activation enthalpy for this level relative to the valence band is 0.13 eV in going from $x=0.0$ to $x=0.25$. Although the increase in activation enthalpy from $x=0.0$ to $x=0.05$ is on the edge of the precision; we speculate whether this small increase in activation enthalpy is due to some residual compressive strain in the $x=0.05$ material as it is very difficult to relax this material completely; we are currently investigating the effect of compressive strain on the Au levels in SiGe. In the Ge-concentration range of the present investigation, the band gap changes by 0.10 eV;[8] hence, the above activation enthalpy values of the acceptor level are indicative of a pinning to the conduction band. From the temperature dependence of the gold acceptor level in Si, Engström and Grimmeiss[9] have concluded, using the spectral distribution of the optical emission rates, that this level is pinned to the conduction band, whereas Samara and Barnes[10] concluded from pressure experiments, that the levels were pinned neither to the valence band nor the conduction band.

There is no indication of an increase in the activation enthalpy of the donor level, displayed in Fig. 4(a), in going from $x=0.0$ to $x=0.05$, as was the case of the acceptor level. There is a gradual decrease of the activation enthalpy relative to the valence band of $\sim$0.12 eV from $E_v+0.314$ eV to $E_v+0.199$ eV in going from $x=0.0$ to $x=0.25$, which is the same decrease as observed for the acceptor level in the p-type material. Thus, using the same arguments as for the acceptor level, it can be concluded that the measurements indicate that the donor level is also pinned to the conduction band. The Au donor level has been studied in bulk crystal $Si_{1-x}Ge_x$ grown by a Czochralski technique, with a Ge content between 0% and 5.4%,[10] and although the investigated Ge content is small, a similar decrease in activation enthalpy with Ge content was found.

Watkins and Williams[11] have recently demonstrated that the electronic structure of substitutional, neutral gold in silicon is similar to that of the isolated, negatively charged vacancy V^-; as a consequence, the acceptor level $(-/0)$ of gold is similar to the $(=/-)$ level of the vacancy, and the donor level of gold $(0/+)$ is similar to the $(-/0)$ level of the vacancy. Van Vechten and Thurmund[12] have argued that both the $(-/0)$ and $(=/-)$ are pinned to the conduction band; hence, following this argumentation, pinning of both the gold acceptor and donor levels to the conduction band would be expected, in agreement with the indication of the present investigation. However, definite proof must await precise, experimental values of the entropy of ionization as a function of Ge content; such measurements are in progress.

The intensity ratio between the Au donor and acceptor level is increasing with increasing Ge content, as seen in Fig. 2; this effect can be qualitatively understood based on a description by Mesli,[13] in which the thermal-hole emissivity is increased as a consequence of the Au acceptor being pinned to the conduction band and thereby moving towards the valence band.

In conclusion, we have demonstrated the feasibility of doping relaxed, MBE grown SiGe alloy layers with gold. We have used this property to study the dependence of the energy levels of the donor and acceptor states of substitutional, neutral gold as a function of Ge content in these alloys. The data indicate that both levels are pinned to the conduction band, in agreement with the ''vacancy model'' of the neutral-gold impurity in silicon, combined with the theoretical prediction that the acceptor levels of the vacancy in Si are pinned to the conduction band. The observed increase in the intensity of the line from the acceptor state in p-type material with increasing Ge content is explained as an effect of the pinning of the acceptor level to the conduction band.

Finally, the ability to dope SiGe layers of high crystalline quality with metal impurities, as demonstrated in the present investigation, opens up for a family of studies where the effect of bandgap changes on deep levels can be studied, and thus theoretical models can be tested.

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