Alloy Splitting of Gold and Platinum Acceptor Levels in SiGe

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Laplace transform deep level transient spectroscopy was used to study the acceptor levels of platinum and gold diffused into dilute (0–5% Ge) SiGe alloys. We show that Ge atoms in the first and in the second shell of atoms surrounding the impurity perturb the electronic properties of the Au and Pt acceptor defects. The magnitude of the splitting caused by one Ge atom in the first shell is ~35 meV in both cases. The spectral distributions indicate an overpopulation of Ge-perturbed sites as compared to randomly occupied sites. This can be quantitatively interpreted in terms of an enthalpy difference of ~60 meV between configurations with zero or one Ge in the first shell surrounding the impurity.

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Deep states of point defects in semiconductor material are characterized by electronic wave functions that are localized on the scale of a few bond lengths. Consequently, their electronic structure will be sensitive to the details of the atomic configuration in the close vicinity of the defect. In the case of random semiconductor alloys, the spatial fluctuations in local alloy composition may cause variations in the thermal emission rates of carriers from the defect and in optical absorption frequencies. This has the consequence that a deep-center energy level, upon alloying, appears to split into a manifold of components. The thermal emission, as opposed to the optical absorption, is sensitive to the lattice relaxation that may accompany the electronic transition. Therefore, if the fine structure of the thermal spectrum is to be interpreted in terms of "alloy splitting" of the bound-state total energy, the effective radius of the bound carrier may be regarded as the crucial parameter. The interpretation of observed fine structure in terms of spatial splitting of total-energy levels is far from straightforward when both initial and final states are alloy sensitive, which happens when the ionization is accompanied with a notable lattice relaxation. However, as long as the alloy is macroscopically homogenous, it may be assumed that the observation of fine structure (or line broadening) in the ionization spectra of defects is a manifestation of spatial fluctuations in the alloy composition on the microscopic scale rather than variations in bulk band-gap parameters.

Alloy splitting of defects in semiconductors has been studied previously in the case of ternary random alloys, such as $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$. Here the alloying occurs only in the group III sites, i.e., in every second shell of atoms surrounding a given atomic site. Thus for the substitutional site on the group III or group V sublattice, the closest mixed atom shell is in the second- or first-nearest neighborhood, respectively. A similar effect is observed for nonequivalent interstitial sites of the zinc blende unit cell. In contrast to this, the alloying occurs in every shell of atoms when Si and Ge are mixed to form a SiGe alloy. In view of the short-range interaction involved, one can expect that only one shell of atoms influences the level splitting in the case of a ternary alloy, whereas for binary alloys such as SiGe two shells may contribute. Partially resolved alloy splitting has been observed by photoluminescence measurements [1] and deep level transient spectroscopy (DLTS) [2] applied to defects in ternary alloys, and more recently by Laplace DLTS [3]. Considering the fact that both first- and second-shell interactions may be of importance in the elemental alloy, we show that the application of Laplace DLTS enables a uniquely detailed mapping of environmental effects on deep centers within dilute SiGe. In the present study, we explore this using the platinum and gold acceptor states. These have been studied previously in great detail for pure Si [4]. In addition, some conventional DLTS results are available for SiGe alloys [5,6]. We show that the Laplace DLTS spectra obtained in measurements using samples of dilute SiGe alloys display a fine structure that can be quantified in terms of alloy splitting.

The measurements were carried out using samples grown by molecular-beam epitaxy (MBE) on (100) Si substrates. The Ge content was varied between 0 and 5 at.% in the 4 μm thick top layers of $\mathrm{Si}_{1-x}\mathrm{Ge}_x$. This was grown on top of compositionally graded buffer layers; details of the growth procedure can be found elsewhere [7]. Samples grown according to this procedure are known to have a low density of dislocations (10^5 cm^{-2})

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and a low concentration of deep levels (10^{12} cm^{-3}). The uniform top layers were n type, doped with 5×10^{15} Sb cm^{-3}. Both p^+n-mesa diodes, formed by mesa etching a 200 nm thick MBE grown p^+-type $Si_{1-x}Ge_x$ top layer, and Schottky diodes, produced by e-gun evaporation of Au through a mask, were used. The dopant metals (either Pt or Au) were diffused into the layers at 800 °C for 24 h. In the case of the mesa diodes this was done through the p^+ layer and in the case of the Schottky diodes prior to diode formation.

A Laplace DLTS spectrum of the $(-/0)$ gold acceptor in a SiGe alloy with 5% Ge is depicted in Fig. 1. The substitutional gold atom has four nearest neighbors, so from the binomial distribution governing the mixing of gold atoms in a random binary alloy the probability of finding a given number of germanium atoms, i.e., 0, 1, etc., out of four neighbors, in the first-nearest shell of Au at a Si substitution site can be calculated. The left-side bars of the inset of Fig. 1 represent these probabilities assuming that they are given by the alloy composition (here 5%). For comparison, the right-side bars in this diagram depict the relative intensities of the measured peaks. This comparison allows us to relate subsequent peaks in the series of defects having 0, 1, or 2 germanium atoms in the first shell surrounding the Au atom. The two sets of bars have been normalized to respect the integrated amplitudes relative to the 0Ge configuration.

The association of the individual peaks to given configurations of atoms around the defect are based on the trend in the intensities and comparison with data obtained for pure MBE-grown silicon. It should be noticed, however; that the relative amplitudes of peaks corresponding to the 1Ge and 2Ge configurations are somewhat larger than expected for a perfectly random alloy. This suggests that during diffusion at 800 °C the gold atoms prefer to occupy sites in the lattice next to germanium. Based on several spectra of the kind displayed in Fig. 1, taken for the 5% Ge case as well as for other samples, we conclude that on average the relative concentration of the 1 Ge configuration is approximately twice as big as would be expected for a random sitting. The site preference of gold can be translated to a crude estimate of an enthalpy difference between the 0 Ge and 1 Ge configurations of $\Delta H_{\mathrm{conf}}^{0/1} = \mathrm{kT}(@800\,°\mathrm{C}) * \ln(2) \cong 60$ meV (disregarding terms other than configuration entropy). A similar energy difference can be obtained for the 1 Ge and 2 Ge configurations.

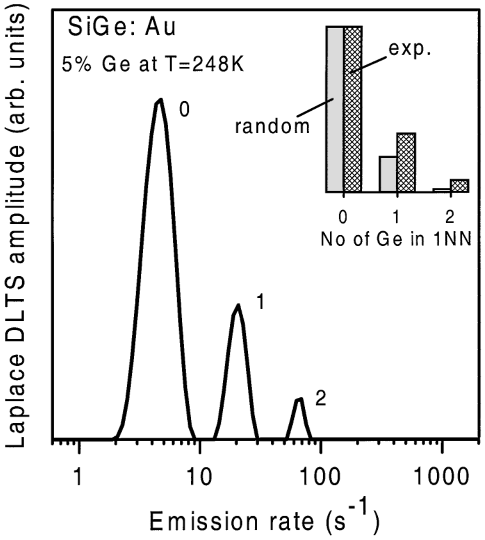

FIG. 1. A Laplace DLTS spectrum of the gold acceptor in a SiGe alloy (5% of germanium). The left-hand side set of bars in the inset show the calculated relative probability of finding a gold atom with 0, 1, and 2 atoms of germanium in the first-nearest shell of atoms assuming a random distribution. The right-hand side set of bars represents the integrated amplitudes of the peaks of the spectrum where the height of the bars is normalized to the 0 Ge configuration in both sets.

While the deviations from the binomial values are indicative of the site preferences that gold atoms take during the diffusion process, the peak positions on the emission rate scale are indicative of how the electronic properties of the acceptor state are modified by alloying. The thermal emission rate (e_{th}) is proportional to the defect capture cross section (σ) and the activation term $\exp(-H_{\mathrm{th}}/kT)$, where H_{th} is the enthalpy of the electron emission. Assuming that the defect in different configurations has the same capture cross section, then the emission rate for the 0 Ge and 1 Ge configurations differ by a factor of ~ 5 (see Fig. 1). This can be related to the differences in the enthalpy for electron emission: $\Delta H_{\mathrm{th}}^{0/1} = \mathrm{kT}(@248\ \mathrm{K}) * \ln(5) = 34$ meV. This energy difference can also be found by evaluating the absolute values of the activation enthalpies for the emission relating to each particular configuration from the Arrhenius plots, i.e., from the $\ln(e_{\mathrm{th}}/T^2)$ versus $1/T$ dependence. This procedure gave for the 5% sample the ionization enthalpies for the 0 Ge and 1 Ge lines equal to 0.58 ± 0.02 eV and 0.55 ± 0.04 eV, respectively. These two values are consistent with the conventional DLTS measurements showing only a slight increase of ΔH_{th} for the 5% sample compared to the value reported for pure silicon [5]. For the samples with lower germanium content the gold acceptor ionization enthalpy (0 Ge line) equals to 0.55 ± 0.01 eV, which is almost identical to the value for pure silicon.

Figure 2 shows the Laplace DLTS spectra for the platinum diffused samples with alloy compositions of 0.5 and 5%. For the 0.5% sample we observe, in addition to the main line (as seen in pure silicon), the appearance of a small satellite line. In the sample having 5% germanium content the spectrum has many more features and does not display a clear series of lines as in the case of the gold diffused sample. It should be noted at this point that both samples were made from pieces of the same 5% Ge wafer.

In order to analyze this observation we must consider both the first and the second nearest neighbors of the

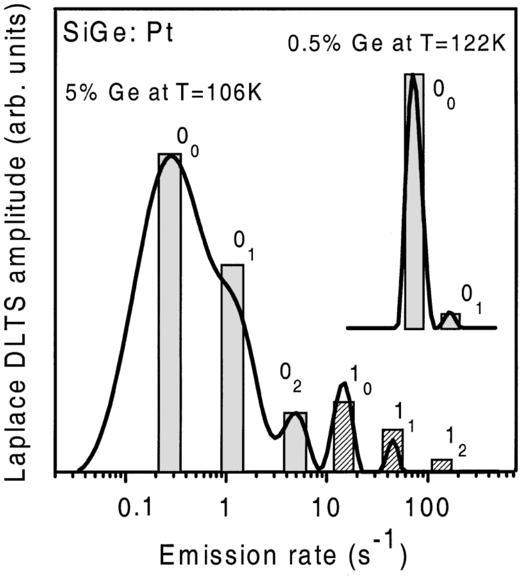

FIG. 2. The Laplace DLTS spectra of the platinum related center in the SiGe alloy (0.5% and 5% of germanium). The figures and subscripts denote configurations with the indicated numbers of germanium in the first and second nearest shell, respectively.

substitution-site Pt impurity. In general, if one assumes that the distribution of germanium atoms in the first nearest shell is truly random, then as there are four atoms in this shell one would expect to have five different configurations. However, for 5% of germanium in the crystal the probability of having more than three germanium atoms in the first shell would be very low. As a result, the influence of the local environment beyond the first shell could be significant for the case of platinum. In the following analysis we will explore the possibility that the second nearest shell of atoms around platinum (an additional twelve) also influences the emission process. Analogous to the previous simulation for the gold case, when two shells of atoms are to be considered, we may assign spectral features to two groups of peaks, those having zero and those having one germanium in the first nearest shell. The bars in Fig. 2 result from such a simulation. The spectral features can be correlated with the bar diagram, each feature being assigned a figure and a subscript denoting the number of germanium atoms in the first and second nearest shell, respectively. For both spectra in this figure the bars representing the probability of finding zero germanium atoms in the first and in the second shell of atoms (the 0_0 configuration) are normalized to the intensity of the main peaks of the spectra.

We can now evaluate (from the data of Fig. 2) the alloy splitting of the platinum related energy level caused by the addition of one germanium atom in the first nearest shell. The result is $\Delta H_{\mathrm{th}} \approx 39$ meV for the energy difference of electron emission from the platinum between the 0_0 and 1_0 configurations, i.e., comparable to the value for gold. When the germanium atom is present in the second nearest shell the splitting is smaller. The energy difference for electron emission between the 0_0 and 0_1 configurations is ~ 12 meV. A similar procedure applied for the case of the 1_0 and 1_1 configurations gives the energy difference for electron emission from these configurations to be around 10 meV. However, it must be emphasized that the 1_1 configuration is not unique. The emission-rate shift (level shift) may depend on whether or not the two germanium atoms of the first and second shell form a direct bond. We may, however, expect this effect to be of second order. For the 1% sample the Laplace DLTS spectrum of the Pt-diffused sample is narrower than this observed for the 5% sample, which allows us to estimate the absolute values of the ionization enthalpies more precisely. This is because measurements over a wider temperature range were possible. We have obtained, for the 0_0 and 1_0 lines, enthalpies equal to 0.221 ± 0.003 eV and 0.190 ± 0.030 eV, respectively, which is in agreement with the estimate obtained from the peak separation for the spectrum shown in Fig. 2. For the 0_1 line we have obtained the value of 0.220 ± 0.010 eV with a similar result for the 0.5% sample, which is rather an inconclusive result for this analysis.

The obvious question arises as to why the influence of the second shell of atoms is seen for the case of platinum but not for gold. In our view this is a manifestation of the fact that the energy resolution of the Laplace DLTS technique is inversely proportional to the temperature at which the spectrum is taken. This means that the method has a factor of 2.5 lower resolution for the gold center than for the platinum center. As a result, the peak assigned to the 0 Ge configuration for the gold center will be broadened by the unresolved splitting of the 0_0, 0_1, and 0_2 configurations which has been partially resolved in the Pt case. In principle, one would expect that the 0 Ge line should be asymmetric; however, due to limitations of the numerical method used for the Laplace transform inversion, this asymmetry will not be seen in the spectra unless the line separation is larger than the resolution of the method (approximately, a factor of 2 in the emission rate difference) [8]. Thus, there appears to be no fundamental difference between the results for the gold and platinum as far as the alloy splitting is concerned. The differences seen in the Laplace DLTS spectra taken may simply be a result of more advantageous experimental conditions in the latter case.

In the case of gold we found a site preference for having Au next to Ge. A similar preference is not evident in the Pt case. This could possibly be an effect of the numerical procedure. For the 5% sample there is a considerable overlap of many peaks, and the procedure is not able to determine the peak amplitudes precisely. However, for the sample with 0.5% germanium content detailed measurements showed that the 0_1 configuration is also observed in an increased concentration, although the effect is weaker than for the 1_0 configuration. This is consistent with the germanium atom being more distant from the transition in the 0_1 configuration, which makes this configuration energetically less favorable compared to the 1_0 configuration (not observed in this sample due to its expected low population).

The site preference (i.e., favoring of a germanium neighborhood for the transition metal), indicated in the case of Au and suggested for Pt, may be related to details of the microscopic mechanism of the diffusion of these metals in silicon. Both transition metals diffuse by the kickout process. The diffusion proceeds as the metal impurity switches between an interstitial position and a substitutional position. The switching is accompanied by the movement of a host atom from the substitutional to the interstitial site. The driving force for the accumulation of substitutional Au or Pt is the removal of the self-interstitial atoms by sinks. Because of the fact that the germanium atom has a larger ionic radius than the silicon atoms, one can expect that it is easier for the metal to kick out the silicon atoms rather than the germanium atoms from their substitutional positions. A smaller interstitial atom would mean that less energy is needed for a local lattice distortion to accommodate an extra atom. Thus, it would cost less energy to create the self-interstitial defect (silicon atom in the silicon host) than the pseudo-self-interstitial center (germanium atom in the silicon host). This preference of an interstitial site by Si will be partially counteracted by the weakening of Ge-substitution-site bonds as compared to Si-substitution site bonds. Moreover, the self-interstitial creation from a site next to Ge may benefit from an easier relaxation (because of the longer and softer Si-Ge bonds) when the metal squeezes its neighbors. As a result of these competing energy terms during diffusion, the metal atoms prefer to reside as Si-substitutional atoms close to Ge. The effect of an elastic interaction between the Si and Ge host atoms during the diffusion process (retarding the removal of interstitial Ge to sinks) may be compared to the well-known diffusion enhancement effect in silicon where the diffusion of smaller atoms via substitutional sites is promoted by the presence of self-interstitials and larger atoms by vacancies [9].

To summarize, the high-resolution Laplace DLTS spectra for gold- or platinum-diffused SiGe samples show an alloy splitting that may be associated with the spatial alloy fluctuations of the total energy of the nonionized Au and Pt acceptor states. It is consistent with an absence of relaxation associated with the carrier emission [10,11]. For the case of platinum we can distinguish between the effect of the level splitting caused by alloying in the first and in the second shell of surrounding atoms. We have found that the electronic energy level is affected by the alloying in the first nearest neighborhood by a factor 2–3 more than by the alloying in the second nearest shell. A clear preference for gold to enter substitutional Si sites adjacent to Ge has been revealed. In accordance with the well-established diffusion kick-out diffusion mechanism this may be interpreted in terms of an enthalpy lowering as a simple result of the fact that both metals are able to replace the host silicon atom more easily in the substitutional position than the germanium atom. As a result, for gold we observed that the germanium atom effectively lowers the local minimum energy for this metal to occupy the substitutional site by approximately 60 meV.

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