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Evolution of E-centers during the annealing of Sb-doped $Si_{0.8}Ge_{0.2}$

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Evolution of the chemical surroundings of vacancy complexes in Sb-doped ([Sb] = 2×10^{18} and 2×10^{19} cm^{-3}) $Si_{0.8}Ge_{0.2}$ was studied with positron annihilation spectroscopy in Doppler broadening mode. The study was performed by annealing the samples both isochronally and isothermally. Defect evolution was observed at the temperature range 450–650 K. Both treatments were shown to induce changes in the chemical surroundings of the E-centers via introduction of Ge near the defects. Moreover, Sb was found to hinder these changes by stabilizing the E-centers and thus preventing them from finding Ge. The stable state reached after the anneals was found to differ from that measured from an as-grown sample. This difference was deemed to be the result of Ge gathering in small clusters during the annealing thus breaking the initially random Ge distribution.

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I. INTRODUCTION

The never-ending striving to build faster devices has brought the microelectronics industry to the edge of its physical limitations when it comes to using silicon as the material for components. As a result, the interest in silicon-germanium ($Si_{1-x}Ge_x$) research has taken leaps during the past few years and benefits of the unique properties of the material can already be seen in device industry. For example, the realization of the 32-nm scaling node[1] was made possible by strain and heterojunction engineering provided by $Si_{1-x}Ge_x$.[2] Point defects in semiconductors often mean trouble as they can influence the electrical and mechanical properties of the material in various ways. $Si_{1-x}Ge_x$ is no exception to that rule and thus understanding the properties of point defects is crucial in order to realize ways for optimizing device performance. It is well known that unwanted point defects form in semiconductors during various device synthesis and processing steps such as ion implantation. Interestingly, ion implantation and/or irradiation can also be used to create controlled amounts of well-specified point defects for defect study purposes. Thanks partially to studies on such irradiation-induced defects, it is now known that vacancy complexes (and vacancy-impurity complexes in the case of high enough impurity content in the material) are fundamental point defects in Si-based materials and a significant effort has been made to study dominant configurations and corresponding electronic signatures.[3,4]

Among all the different point defect types in semiconductors, one of the most studied is the E-center in Si. It consists of a vacancy and a group-V donor impurity (As, P, or Sb). Besides influencing the electrical properties of the material, the E-center has also been shown to affect the migration of impurities (dopants) in Si.[5,6] In pure Si, two energy levels have been found for the E center: an acceptor level at $E_C - 0.45$ eV,[7] and a donor level at $E_V + 0.27$ eV,[8] where E_C and E_V are the conduction and valence bands of the material, respectively. In the case of pure Ge, two acceptorlike energy levels and one donor level have been associated with E-centers.[9–11] In the wake of the recent interest in $Si_{1-x}Ge_x$, a number of studies on the E-center have been conducted also in this material.[12–18] While the contribution of these studies to the understanding of E-centers in $Si_{1-x}Ge_x$ has been significant, the fundamental picture of the defects is still lacking. Particularly, experimental documentation is insufficient and the existing works are largely based on high-temperature dopant redistribution measurements, which always take the inevitable risks of modifying the delicate $Si_{1-x}Ge_x$ matrix itself.

The purpose of this work is to study the annealing behavior of E-centers in Sb-doped $Si_{1-x}Ge_x$ and to compare the results with those from P-doped material[18] and from pure Si.[6] The E-center annealing is measured in relaxed and proton irradiated $Si_{1-x}Ge_x$ layers using positron annihilation spectroscopy.

II. EXPERIMENTAL METHOD

A. Positron annihilation spectroscopy

Positron annihilation spectroscopy (PAS) is a versatile tool for studying vacancy-type defects in various materials.[19,20] The atomic resolution provided by the annihilation radiation provides information about the defects themselves as well as the atoms in their near vicinity. The use of slow, monoenergetic positrons allows the study of defect distributions in thin layers.

In this work, we used a monoenergetic slow positron beam in Doppler broadening mode to study the defect and bulk properties of relaxed $Si_{0.8}Ge_{0.2}$ layers. The fast positrons emitted by a ^{22}Na source were moderated with a 1-μm tungsten foil, accelerated with an electric field and then implanted into the sample at desired energies ranging from 0.5 to 35 keV. After implantation, the positron thermalizes rapidly in the sample, the thermalization time being in the order of a few picoseconds. Following thermalization, the positron diffuses in the sample for 100–250 ps (tens to hundreds of nanometers depending on material and the defects present) before finding an electron and annihilating.[19,20] Positrons can get trapped into neutral and negatively charged open volume defects in the sample. Particularly, open volume defects such as vacancies act as efficient positron traps. Such defects can be characterized by increased positron lifetime in lifetime measurements and a narrower momentum distribution in Doppler broadening measurements.

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In positron Doppler broadening spectroscopy, the broadening of the 511-keV annihilation line due to the momentum of the annihilating electron-positron pair is detected. We used two high-purity Ge detectors with an energy resolution of 1.2 keV at the 511-keV line to detect the annihilation quanta and measure their energies. At the moment of annihilation two 511-keV annihilation quanta are emitted at almost the opposite directions, with a slight angular difference induced as an additional effect of the momentum of the annihilating pair being conserved in the process. The use of two Ge detectors makes it possible to measure the annihilation events in coincidence, requiring signals from both detectors in order to register an event. With this technique, the peak-to-background ratio can be improved to roughly 10^6 at the expense of the count rate. The usage of coincidence Doppler broadening (CDB) mode enables us to study the momenta of the core electron region very accurately, allowing the identification of the chemical surroundings of defects at which the annihilations occur.

In the standard Doppler broadening measurements, conventional line-shape parameters S and W were used to describe the results. The S parameters, also often referred to as the low-momentum parameter, is defined as the fraction of counts in the central part of the annihilation peak. The high-momentum parameter W, analogously, tells the fraction of counts in both wings of the annihilation peak and corresponds mainly to annihilations with core electrons. The energy windows for both parameters are normally chosen so that the sensitivity of both is at maximum when it comes to changes in the annihilation environment. In this work, the windows were set to $|p_z| < 0.44$ a.u. for S and 1.60 a.u. $< |p_z| < 4.10$ a.u. for W. The reduced electron density at open volume defects narrows the Doppler-broadened spectrum. Thus an elevated S (or lowered W) parameter typically indicates the presence of open volume defects in a sample.

The measured line-shape parameters S and W are always superpositions of the S and W parameters of different positron states in the sample. In the simplest case, there are only two possible annihilation states (surface and bulk, or bulk and a defect) and the measured parameters can be obtained from

$$S = \eta_1 S_1 + \eta_2 S_2, \quad (1)$$
$$W = \eta_1 W_1 + \eta_2 W_2, \quad (2)$$

where S_i (W_i) is the S (W) parameter of state i and η_i the annihilation fraction in state i. The fact that the equations above are parametrized equations of lines in the (S, W) plane is very useful; plotting the measurement results in the (S, W) plane and analyzing the slopes of the aforementioned lines helps in identifying the defects present. Also, any nonlinear behavior in an (S, W) plot is an indication of three or more positron annihilation states in the sample.

B. Samples

We studied relaxed 4-μm $Si_{0.8}Ge_{0.2}$ layers doped with 2×10^{18} and 2×10^{19} Sb/cm^{-3}. The SiGe layers were grown on p-type, (001) Si substrates using molecular-beam epitaxy. A graded SiGe buffer was included between the substrate and the $Si_{0.8}Ge_{0.2}$ top layer in which the Ge concentration was increased from 0 to 20% at a rate of 10% per micrometer. This buffer layer was grown at a temperature of 820 K, and the $Si_{0.8}Ge_{0.2}$ top layer was grown at a slightly lower temperature of 690 K, in order to allow for the incorporation of the high Sb concentrations. The growth rate was 2 Å/s. The used growth parameters are known to produce $Si_{0.8}Ge_{0.2}$ layers with threading dislocation densities lower than 5×10^5 cm^{-2}. The samples were irradiated with 1.8-MeV protons, creating a homogenous defect distribution within the $Si_{0.8}Ge_{0.2}$ layer in order to ensure that the characteristic positron parameters were constant throughout the layer. The proton fluence (10^{15} cm^{-2}) used in the irradiation was high enough to produce saturated positron trapping, i.e., a defect concentration $\gtrsim 10^{18}$ cm^{-3}, and the defects were identified as V-Sb pairs (E-centers).[17]

In order to study the evolution of the E-centers, both isochronal and isothermal annealings were performed on the samples. The procedure for isochronal annealing was to ramp up the temperature in steps of 50 K, starting from 350 K, keeping the sample at each temperature for 30 min and measuring the positron parameters between the steps. The final temperature for isochronal annealing was 800 K. Isothermal annealings were done at two temperatures: 450 and 600 K. The annealing time steps were 60 min at 450 K and 30 min at 600 K. The positron parameters were again measured between the annealing steps. All measurements in both experiments were performed at room temperature and the obtained positron parameter values were normalized to the respective values (S_{SiGe}) of as-grown samples.

III. RESULTS

A. Annealing experiments

Figure 1 shows the S and W parameters as a function of annealing temperature in the isochronal experiment for both

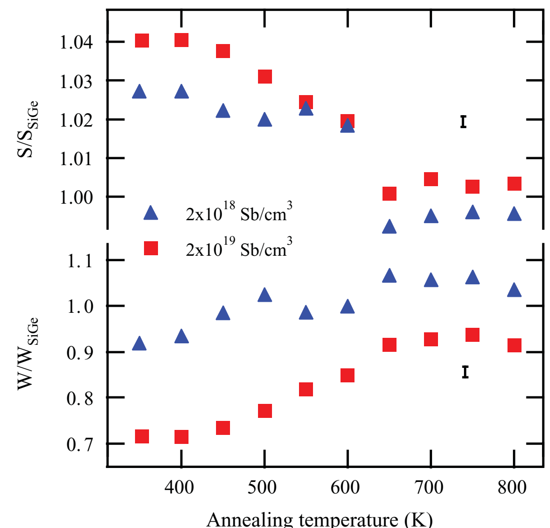

FIG. 1. (Color online) The low-momentum parameter S (upper panel) and the high-momentum parameter W (lower panel) as a function of annealing temperature in samples isochronally annealed at steps of 30 min. The values have been scaled to those of as-grown $Si_{0.8}Ge_{0.2}$. The typical error of the parameters is also indicated.

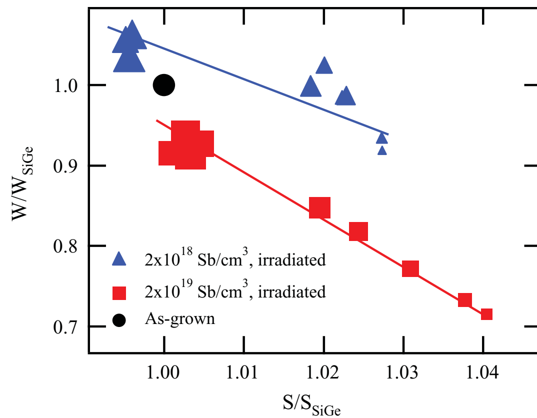

FIG. 2. (Color online) The (S,W) parameters measured in isochronally annealed $Si_{0.8}Ge_{0.2}$ samples. The data have been scaled to the values of as-grown $Si_{0.8}Ge_{0.2}$. Increasing symbol size represents increasing annealing temperature. The lines are drawn to guide the eye.

Sb concentrations. The annealing trend is the same in both cases. The defects start to anneal at around 450 K and the process is slow until 600 K. Between 600 and 650 K there is a sharp drop in the S parameter indicating rapid annealing of the defects. The state reached after this drop seems to be stable as the parameters did not change at all while further increasing the annealing temperature. The W parameters do not exhibit the sharp change between 600 and 650 K but otherwise they behave analogously to their S counterparts; the changes start at 450 K and a stable state is reached at 650 K. Interestingly, this stable state differs from that obtained from as-grown material, with differences mainly showing in the W parameter.

The (S,W) parameters shown in Fig. 2 reveal that the stable state reached after the isochronal annealing clearly differs from that of the as-grown sample in both cases, indicating permanent change in the samples as a result of the treatment. The differences being mainly in the W parameter suggest a change in the chemical surroundings of the annihilation sites. An elevated W parameter is a sign of increased Ge decoration of the defects,[15,17] which is the case with the lower Sb concentration. In the sample with more Sb, on the other hand, W falls below the as-grown value, indicating that Sb also has a role in the lattice evolution.

In Fig. 3, the $(S,\ W)$ parameters are shown for the isothermal annealing experiments. Even after only a few hours of annealing, it is clear that the trendlines point toward a state different from the as-grown one. Another interesting fact is that in both samples, the W parameter stays higher when the isothermal annealing is performed at a lower temperature. This can be explained with Ge decorated E-centers which are more likely to be present at low temperatures and thus more annihilations occur with Ge core ($3d$) electrons.

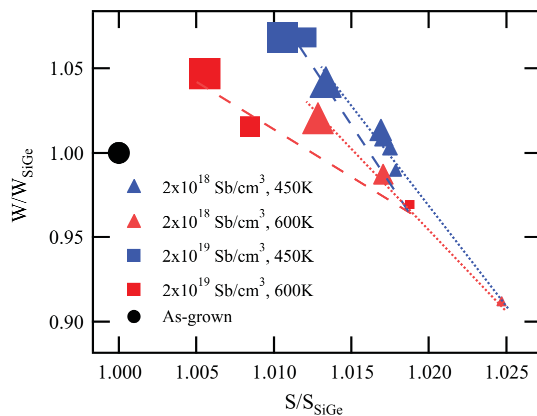

FIG. 3. (Color online) The (S,W) parameters measured in isothermally annealed $Si_{0.8}Ge_{0.2}$ samples. The data have been scaled to the values of as-grown $Si_{0.8}Ge_{0.2}$. Increasing symbol size represents increasing annealing time. The lines are drawn to guide the eye.

B. Coincidence Doppler broadening measurements

Figure 4 shows the coincidence Doppler broadening spectra measured from as-irradiated and annealed samples, along with theoretical momentum distributions of V-Sb and V-Sb_2 complexes in silicon.[21] The high ratios seen at high momenta are a fingerprint of Ge $3d$ electrons, indicating the presence of V-Sb-Ge_n complexes. The difference in the momentum distributions of the isochronally annealed samples shows that Sb stabilizes the defects and prevents them from finding Ge rich areas in the material. The Ge effect in the sample doped

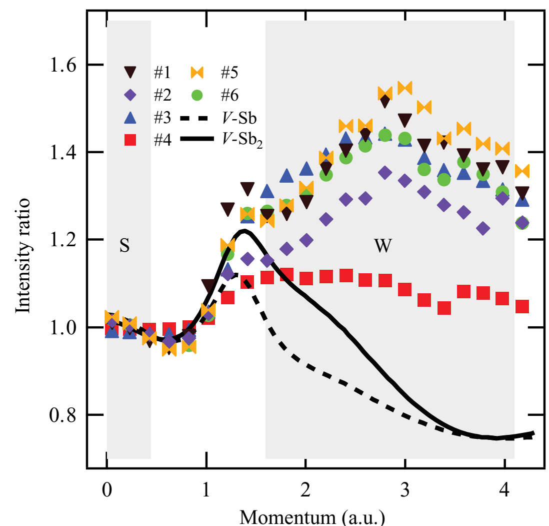

FIG. 4. (Color online) The momentum densities of as-grown and annealed $Si_{0.8}Ge_{0.2}$ samples along with theoretical calculations for V-Sb and V-Sb_2 defects in Si. All densities have been scaled to that of bulk silicon. Samples 1 and 2 are as-irradiated ones with 2×10^{18} Sb/cm^{-3} and 2×10^{19} Sb/cm^{-3}, respectively. Samples 3 and 4 are the same annealed isochronally at 800 K. Samples 5 and 6 have been isothermally annealed for 3 h at 550 K.

with 2×10^{18} Sb/cm^{-3} at very high momenta is more or less the same after and before the annealing treatment whereas in the other sample the ratio in that region drops drastically as a result of the annealing. Another feature of interest in the data from isochronally annealed samples is that the low-momentum (S parameter) region is very close to that of bulk Si, suggesting that the stable end state reached after the isochronal annealings is in fact defect free but the lattice itself looks different from a positron's point of view—most likely due to the germanium being accumulated in small clusters instead of being randomly distributed as is the case in as-grown samples. Similar behavior was previously observed in P-doped $Si_{1-x}Ge_x$.[18]

IV. DISCUSSION

The annealing behavior of E-centers with P and Sb as dopants has now been studied with positrons both in pure Si (Refs. 6 and 21) and in $Si_{1-x}Ge_x$ (Refs. 17 and 18 and this paper). Thanks to positron Doppler broadening spectroscopy being sensitive to the chemical surroundings of defects, it has been possible to monitor the evolution of the E-centers throughout the annealing process in these materials. The interpretation of the results requires knowledge of how each change in the chemical environment of the E-center affects the positron parameters.

In Fig. 5, schematics of E-center evolution during isochronal annealing of both Si and $Si_{1-x}Ge_x$ are shown for P- and Sb-doped materials. In Si, the defect evolution is quite straightforward since the only possible change can occur in the numbers of Si and dopant atoms around the defect. As shown in Fig. 5, the E center can accumulate up to two additional phosphorus atoms around it in Si. Both of these changes are seen as a slightly lower S parameter whereas W stays more or less constant. In Sb-doped Si, only the conversion from V-Sb to V-Sb_2 was observed with positrons. This occurs at above 600 K and is seen mainly as a considerable increase in the W parameter. The S parameter is lowered slightly also in this case. The third group-V dopant commonly used in these materials—As—is not included in the figure as its $3d$ electrons are similar to those of Ge and thus it is difficult to distinguish between the two elements in positron Doppler broadening measurements in the case of $Si_{1-x}Ge_x$. In Si : As, the annealing behavior is analogous to that of Si : P.[6]

In $Si_{1-x}Ge_x$, the situation is slightly more complex when it comes to defect evolution during annealing as, in addition to the dopant atoms, there are also Ge atoms present in the lattice. Fortunately, Ge $3d$ electrons have a very strong characteristic signature when probed with positrons. In the case of P-doped $Si_{1-x}Ge_x$ it is mainly Ge that contributes to changes in the positron parameters since P is very similar to Si, both having a $2p$ outer shell. The accumulation of Ge around the defects is easy to see from a considerably higher W (and slighly lower S) parameter for each additional neighboring Ge atom. During isochronal annealing, only complexes with one Ge atom could be detected, and higher Ge decoration could only be achieved

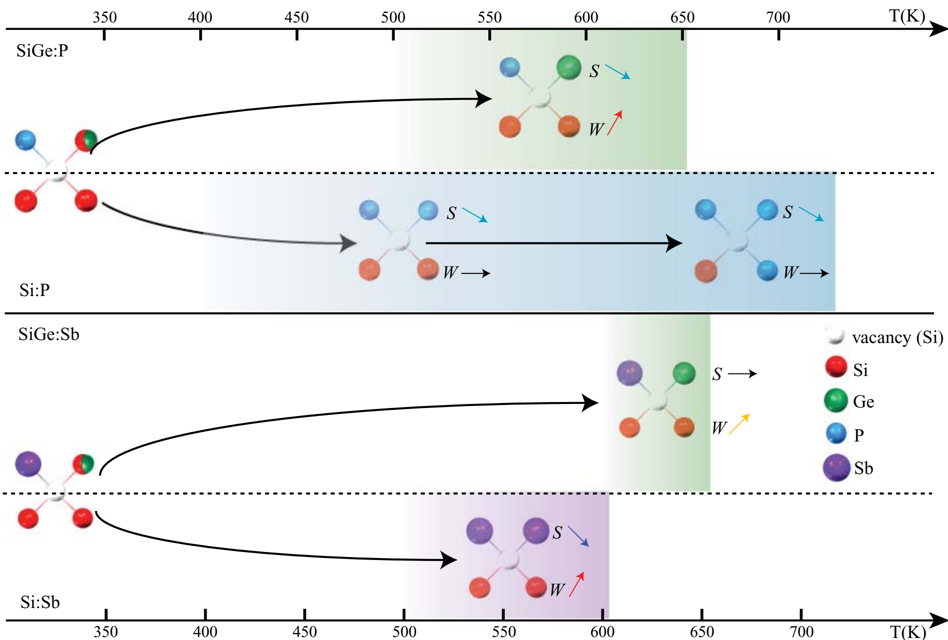

FIG. 5. (Color online) The evolution of E-centers in P- and Sb-doped Si and $Si_{1-x}Ge_x$ as a function of temperature in isochronal anneals. The highlighted areas show the temperature ranges for observing the defects shown within the highlight. Alongside each defect illustration, the evolution of positron parameters compared to the previous step in the process is shown with arrows. The half-red, half-green (two shades of gray) atom in the initial states indicates that in $Si_{0.8}Ge_{0.2}$ roughly half of the E-centers have at least one Ge atom as a nearest neighbor.

with lengthy (from a couple to tens of hours depending on the temperature used[18]) isothermal anneals.

Sb-doped $Si_{1-x}Ge_x$ is the most complicated case out of the four materials presented here since both Ge and Sb greatly influence the positron parameters. The effect of additional Ge is similar to that in P-doped $Si_{1-x}Ge_x$, and also in this case, Ge decoration of two or more atoms is seen only after isothermal anneals. It is also worth noting that the second Ge atom seems to affect the positron parameters more in this case, whereas in P-doped $Si_{1-x}Ge_x$ each additional Ge has an effect of similar magnitude. Sb affects the parameters in the same way as Ge does; W increases and S slightly decreases. However, the changes due to additional Sb are smaller than those due to Ge. This can be largely attributed to the W window (see Fig. 4) covering the Ge effect at 3 a.u. in its entirety whereas most of the Sb peak at 1.2 a.u. does not contribute to W at all. In this work, complexes with more than one Sb atom could not be observed but Sb still affected the evolution of the defects. The isothermal annealing experiments showed that samples with higher Sb concentration did not express as much Ge accumulation around the defects as those with less Sb. Thus Sb seems to act as a stabilizer for the E-centers and prevents them from finding Ge rich areas in the samples.

V. SUMMARY

In conclusion, we studied the thermal evolution of E-centers in Sb-doped $Si_{0.8}Ge_{0.2}$ by applying positron annihilation spectroscopy in Doppler broadening mode on both isochronally and isothermally annealed samples. The isochronal experiment showed the defect annealing to occur at the temperature range 450–600 K. The state reached after the annealing is stable but different from that of an as-grown sample as can be seen from Fig. 2. The differences are mainly in the W parameter and thus imply changes in the chemical surroundings of the annihilation environment. The way the W parameter behaves suggests the presence of both Sb and Ge around the annihilation sites. The isothermal annealing experiment also indicates changes in the chemical surroundings of the defects throughout the annealing process, with elevated W being a sign of Ge atoms near the E-centers. These Ge-rich E-centers are more stable at lower temperatures which is also seen from the results; the W parameters stay constantly higher in samples annealed at lower temperatures. Finally, the coincidence measurements confirm the existence of both Ge and Sb in the close vicinity of the E-centers. Sb is shown to stabilize the defects and to prevent them from finding Ge-rich areas in the sample. The coincidence results also reveal the end state reached after isochronal annealing to be nearly defect-free, indicating that the differences to the as-grown state are in fact caused by germanium being in small clusters after the annealing rather than randomly distributed.

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