junctions. The results are in qualitative agreement with the theory of Feldman *et al.* The high reproducibility of well-controlled Josephson tunnel junctions facilitates their use in SUPARAMP'S and we feel that they exhibit high promise for use in future practical devices.

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Effects of ion-implanted atoms upon conduction electron spin resonance (CESR) in a Si:P system

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The behavior of the conduction electron spin resonance of ion-implanted (Si:P):Sb and (Si:P):Te systems is observed to be strongly modified by the presence of Sb or Te substitutional atoms in shallower surface layers; i.e., the ESR signal shows an anomalous line broadening. The origin of the anomalous broadening may be due to the spin-orbit interaction between the conduction electrons contained within a thin layer ($\leq$25 μm) and implanted Sb or Te impurities contained within a thin layer ($\doteq$0.1 μm).

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We have done ESR measurements on spin systems which include ion-implanted atoms. The conduction electrons in this system arise from implanted phosphorus (P) donor atoms. Another impurity atom (X) is implanted in the silicon crystal after implantation of P and annealing in order to investigate the interaction with the conduction electrons. In the previous paper,[1] it was shown that an ion-implanted Si:P system has essentially the same donor-concentration dependence of the ESR as phosphorus-doped bulk silicon (bulk Si:P). The effective spin-lattice relaxation time in ion-implanted Si:P was also found to be unaffected by scattering at the surface or the interface of the p-n junction. In this paper we report that the behavior of the conduction electron spin resonance (CESR) of Si:P is observed to be strongly modified by the presence of certain atoms in the shallower surface layer. We also discuss several possible explanations for this phenomenon.

Phosphorus ion implantation was done at an energy of 200 keV with doses of 5×10^{13} to 3×10^{15} P/cm^2 at room temperature. The samples were annealed in a vacuum of about 10^{-6} Torr at 900 °C for 15 min in order to obtain substitutional P in damage-free Si (Si:P). The implanted profile dispersed by annealing is $\Delta x = (4Dt)^{1/2} \doteqdot 600$ Å. After annealing, one of the different impurity atoms X ($_7$N, $_{18}$Ar, $_{25}$Mn, $_{30}$Zn, $_{33}$As, $_{48}$Cd, $_{49}$In, $_{51}$Sb, and $_{52}$Te) was implanted at room temperature into ion-implanted Si:P at 35–60 keV with doses between 1×10^{13} and 1×10^{14} X/cm^2. In order to investigate the dose dependence for Sb, 40-keV Sb were implanted with doses of 10^{10} to 10^{13}/cm^2. 40-keV Sb atoms with a dose of 1×10^{15}/cm^2 were also implanted into bulk Si:P with a donor concentration of about 1.5×10^{19} P/cm^3. Implanted samples were annealed again in order to eliminate the radiation damage and achieve ion-implanted (Si:P):X systems. The ESR measurements were made

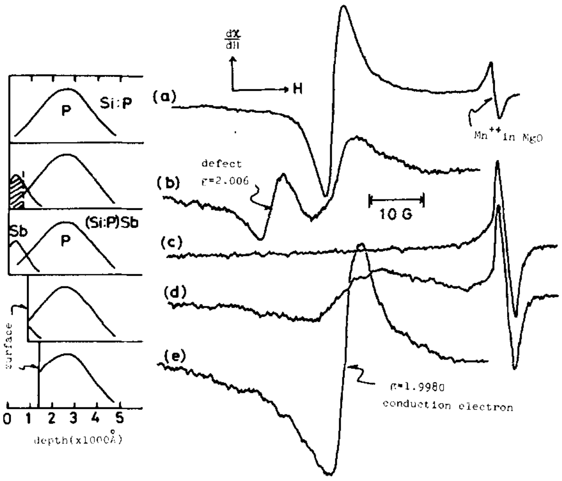

FIG. 1. ESR spectra and the schematic profile of P and Sb in Si : P and (Si : P) : Sb systems. The maximum values of P and Sb donor concentration are about 4.4×10^{19} cm^{-3} and 1.6×10^{19} cm^{-3}, respectively. Part shaded with oblique lines indicates damaged regions.

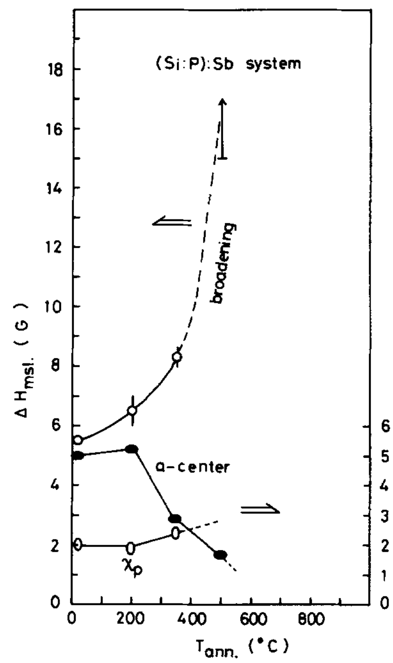

FIG. 2. Isochronal annealing of ESR linewidth and χ_p of conduction electrons, and the number of the amorphous center.

with an X-band spectrometer using 100-kHz modulation at liquid N_2 temperature. The recorded data were the derivative of the absorption signal, which is proportional to $d\chi''(H)/dH$. The ESR of ion-implanted (Si : P) : Sb was measured before annealing and after annealing at various temperatures. The removal of the surface layer was done by using anodic oxidation and chemical etching techniques.[2] The thickness removed per stripping step was about 100 Å. The ESR measurements were made after each removal.

Figure 1 shows the ESR spectra and the schematic profile of P and Sb atoms at each step in our measurements of the (Si : P) : Sb system. Implanted doses were 1×10^{15} P/cm^2 for 200-keV phosphorus ions and 4×10^{13} Sb/cm^2 for 60-keV antimony ions. As shown in Fig. 1(a), the ESR signal of the conduction electrons in ion-implanted Si : P has a single Lorenzian line shape with a g value of 1.998.[1,3] When Sb ions are implanted into Si : P, localized amorphous regions and damaged regions are produced around ion tracks[3,4] and the electrons of P donors are trapped by them. The ESR signal of the amorphous layer was observed at a g value of 2.006.[1,4] After annealing above 200 °C, the system showed an anomalous broadening of the linewidth ΔH_{msl} as shown in Fig. 1(b) (350 °C anneal) and Fig. 1(c) (900 °C anneal) in spite of the large difference in the depth profiles of P and Sb atoms. Figure 2 shows the annealing behavior of the spin paramagnetic susceptibility χ_p and ΔH_{msl} of the conduction electrons, and the number of the amorphous center[4] in the same sample (200-keV P^+ $1\times10^{15}/cm^2$ and 60-keV Sb^+ $4\times10^{13}/cm^2$). For (Si : P) : Sb annealed above 500 °C, the ESR signal could not be observed because of extreme broadening, but after removing 900 Å, the signal was again observed with a 12-G linewidth, ΔH_{msl}, as shown in Fig. 1(d). After all the Sb implanted layer was removed (1400 Å thick), the linewidth recovered to nearly its original value of 6 G for ion-implanted Si : P [Fig. 1(e)]. Thus, the influence of substitutional Sb atoms on the phosphorus free conduction electron resonance extends beyond the Sb atoms over distances in excess of 2200 Å.

Figure 3 shows the Sb dose dependence of the ESR linewidth ΔH_{msl} of (Si : P) : Sb and the additional linewidth $\Delta H_{add}[=\Delta H_{msl} - \Delta H_{msl}(\text{Si:P})]$. The sample implanted with a dose of 1×10^{14} P/cm^2 has an effective donor concentration of 3×10^{18} P/cm^3, which corresponds to the intermediate region for donor concentrations. The observable broadening starts at about 5×10^{10} Sb/cm^2, which corresponds to a ratio of Sb to P of 5×10^{-4}. The extreme broadening occurs for doses $\gtrsim 10^{12}$ Sb/cm^2, corresponding to a Sb-to-P ratio of about 10^{-2}. At a dose of 2×10^{12} Sb/cm^2, we could not observe the CESR signal. The broadened linewidth is estimated to be more than 15—20 G as deduced from the sensitivity of our apparatus and the number of donor atoms. ΔH_{add} seems to increase linearly with Sb dose in the low-dose range.

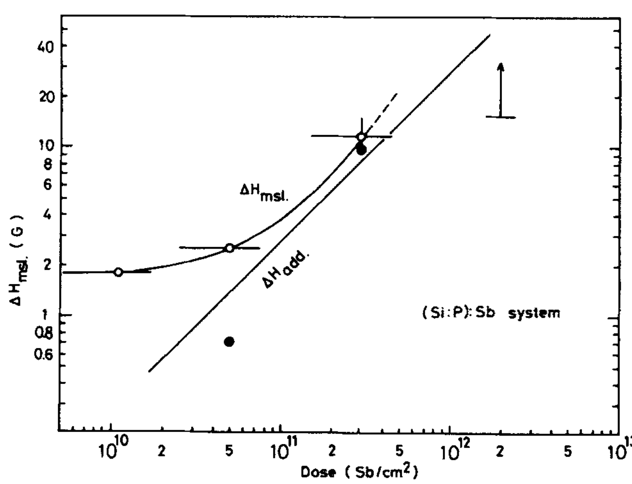

FIG. 3. Sb dose dependence of the CESR linewidth ΔH_{msl} (○) and the additional linewidth ΔH_{add} (●). ($N_D^* = 3\times10^{18}$ P/cm^3) (Ref. 1). Implanted samples were annealed at 900 °C for 15 min.

TABLE I. Additional linewidth ΔH_{add} at liquid N_2 temperature in an ion-implanted (Si : P) : X system.

X atom	Intermediate	Metallic region	Energy (keV)	Dose (cm^{-2})
$_7N$	No broadening	No broadening	50	$1-10\times10^{13}$
$_{18}Ar$		1.5 ± 1.5 G	50	1.2×10^{14}
$_{25}Mn$		± 0.5 G	60	1.3×10^{13} 1.2×10^{14}
$_{30}Zn$	0.2 G		40	1×10^{13}
$_{33}As$	1.2 G		45	1×10^{13}
$_{48}Cd$	0.3 ± 0.2 G		60	2×10^{13}
$_{49}In$	0.3 G		50	2×10^{13}
$_{51}Sb$	Extreme broadening	Extreme broadening	35—60 35—60	1×10^{13} 1×10^{13}
$_{52}Te$	Extreme broadening	Extreme broadening	60	1×10^{13}

This result suggests that observed line broadening may possibly be explained by the modified Pines model.[5]

The results of the additional line broadening ΔH_{add} at 77 K in the (Si : P) : X system are given in Table I for the intermediate and high donor concentration regions.[1] ΔH_{add} was less than 0.5 G in (Si : P) : N, : Mn, : Cd, and : In systems and was 1.2 G in the (Si : P) : As system, but (Si : P) : Sb and (Si : P) : Te systems showed anomalous line broadening. For the group-V atoms, N, As, Sb, Te, ΔH_{add} increases with the atomic number. From these results, we can say that group-V atoms with a large atomic number induce the anomalous line broadening, but acceptor atoms (Cd and In) with a large atomic number do not. It should also be emphasized that the broadening occurs in spite of the large difference in the depth profiles of P and Sb or Te atoms.

Sb ion implantation in both surfaces of bulk Si : P with a thickness of about 50 μm was observed to have the same effect; i.e., the spin-lattice relaxation time of the conduction electrons is shortened by the presence of Sb donor atoms within the surface layer of several hundred angstroms. A similar phenomenon involving the modification of the CESR by a thin layer has also been reported for copper by several authors.[6,7]

Although the physical mechanism which accounts for the anomalous line broadening is not yet established, we have considered several possibilities. These possibilities are (1) effects due to internal strain from implanted impurity atoms and/or residual lattice defects, which induce g-value variations, i.e., the inhomogeneous broadening, or shorten spin-lattice relaxation times, (2) effects due to hyperfine interactions with nuclei of impurity atoms which cause inhomogeneous broadening, and (3) effects due to the spin-orbit coupling between conduction electrons and impurity atom which admix spin states and cause spin-flips. We think the first one can be ruled out because the line broadening is observed to be reasonably independent of the size of atom and because the strain induced around the damage regions does not affect the ESR linewidth of the conduction electrons. The second possibility appears unlikely because the anomalous line broadening occurs for Te even though 92.1% of all Te atoms have zero nuclear spins. The third possibility is not impossible, although the acceptor atoms (Cd and In) with a large atomic number do not induce the anomalous line broadening. However, acceptor atoms which have trapped a donor electron in Si : P would be negatively charged and cause a repulsive potential around the acceptor atoms. Therefore, the conduction electrons would tend to be repulsed by negatively charged acceptors and would not tend to interact with the negatively charged impurities through the spin-orbit interaction. On the other hand, in the case of donor atoms, a conduction electron is delocalized but is always near a donor atom in order to provide charge compensation. The conduction electrons experience the spin-orbit coupling to certain impurity atoms, which cause the relaxation of the Zeeman energy by a spin-flip. In this case, the anomalous line broadening involves a direct physical interaction between the conduction electron and certain impurity atoms.

Clearly more work is needed in order to clarify the mechanism which account for these unusual and interesting results.

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