Observation of Co-Dimer Formation during Thermal Annealing of Co-Implanted Si

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The formation of Co dimers is observed in a Mössbauer-spectroscopy study of the thermal annealing of Co-implanted Si. The amount of dimers is found to depend strongly on the annealing temperature, on the implantation dose, and on the Si doping. At measuring temperatures between 4 and 300 K electronic relaxation effects are observed.

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The behavior of transition-metal impurities in semiconductors has drawn increasing attention in recent years[1] both from a fundamental and from an applied point of view. It was noticed, for example, that Si is easily contaminated unintentionally with transition-metal impurities during annealing treatments.[2] These impurities affect the electrical properties of the semiconductors as they are known to produce deep levels in the Si band gap,[3] and to form pairs with acceptor-type dopants.[4] Another reason for the increasing attention is the possible use of epitaxial transition-metal silicides in the making of contacts in semiconductor technology.[5]

The behavior of Co in Si is characterized by two particular properties. First, the diffusion coefficient of Co in Si is found to be so extremely high, and the solubility so low (less than 1 atom/cm^3 at room temperature) that even fast thermal quenching cannot avoid the formation of Co precipitates. The fact that Co atoms cannot be quenched into simple lattice locations is responsible for a second typical property of Co in Si. A critical study[1] of the reported data on the impurity energy levels within the band gap reveals that for Co none can reliably be related to any well-defined defect configuration.

Mössbauer spectroscopy on impurity atoms in host materials offers the fairly unique possibility to characterize the microscopic lattice-configuration surroundings of the probe atom in a wide range of experimental conditions. The method still works where diffraction methods fail because of the presence of lattice damage, or when other methods cannot be used because they require the presence of electrical activity, unpaired electrons, or large concentrations of impurity atoms.

Co atoms in Si can be studied by Mössbauer spectroscopy through ^{57}Co, the parent of the ^{57}Fe nucleus, by far the most widely studied Mössbauer isotope because of its resolution and applicability in a wide temperature range. Spectra originating from ^{57}Co diffused into Si were reported long before the role of Co precipitates was realized. Most of the recent work on diffused ^{57}Co into Si is from Bergholz and co-workers[6] and Dézsi *et al.*[7] in which the role of various Co precipitates is clearly recognized.

The behavior of Co atoms in Si is quite different in implantation experiments. The formation of Co precipitates is avoided because the Co atoms are immobilized by the damage produced in their own collision cascade, as long as the implantation damage is not removed in annealing treatments. For Mössbauer studies on such systems radioactive ^{57}Co has to be implanted. A major difficulty in the production of such beams is the presence of contaminating ^{57}Fe ions, which forces one to use large implantation doses (typically larger than the total amorphization dose for Si, which is around 10^{14} atoms/cm^2) in order to obtain reasonable source strengths. The isotope separator used in these studies was specially modified to deliver an almost ^{57}Fe-free ion beam, mainly by avoiding all Fe-containing parts in the ion source. In this way implantation doses as low as 10^{10} atoms/cm^2 could still be studied.

The Mössbauer spectra obtained from these ion-implanted ^{57}Co sources were discussed in previous papers.[8] The observed implantation dose dependence was interpreted in favor of a direct single-track amorphization model.[9] The microscopic surroundings of the implanted ^{57}Co probe atom were also followed as a function of annealing temperature from the as-implanted "amorphized" site to the surface segregated CoSi$_2$ layer through a number of ill-defined intermediate Co-silicide formation steps.

In this Letter we want to report on the observation of an unusual spectrum component that was missed in earlier studies, because it is present only in a narrow annealing temperature range. It shows a strong dependence on implantation dose and on the type of doping of the semiconductor material. It also shows unusual electronic relaxation effects at low measuring temperatures. We will interpret this spectrum component as due to Co dimers.

Figure 1 shows the room-temperature measured Mössbauer spectra of sources of ^{57}Co implanted into Si and annealed to 475 °C for 1 h in argon atmosphere. The central doublet in these spectra falls in the typical velocity range of Co-silicide spectra, and was therefore attributed[8] to precipitates inside Si. A discussion of the exact nature of the different Co silicides contributing to this central part of the spectrum will not be attempted here. We will only mention a very recent transmission electron microscopy and Mössbauer spectroscopy study of Bergholz *et al.*[10] who report the existence of sandwichlike structures in these precipitates, containing stacks of Si planes enclosed by $CoSi_2$ planes.

This paper deals only with the hitherto unreported side wings in this spectrum, completely outside the velocity range described above. They form a quadrupole doublet with a quadrupole splitting (QS) of 2.65(5) mm/s and an isomer shift (IS) of +0.17(3) mm/s, when converted to an absorber IS with respect to α-Fe. The intensity of this doublet depends on the annealing temperature, the implantation dose, the Si doping, and the measuring temperature.

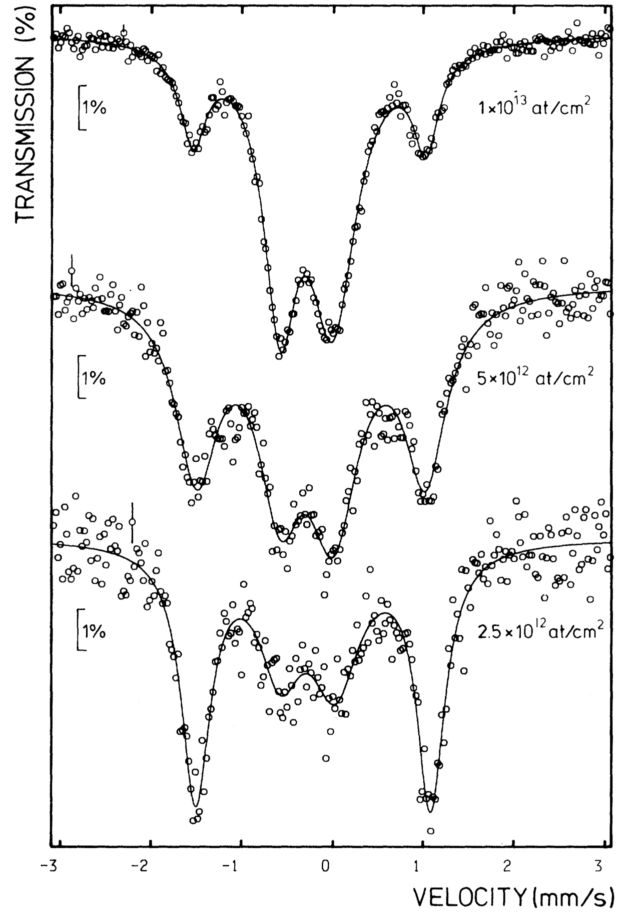

FIG. 1. Mössbauer spectra from ^{57}Co sources implanted into *n*-type Si with various doses, and annealed to 475 °C.

Annealing temperature.—This doublet is only present in a narrow annealing temperature range as shown in Fig. 2. We studied thermally annealed Co-implanted Si samples also by Rutherford backscattering spectroscopy, and found that this temperature range between 450 °C and 500 °C coincides exactly with the recrystallization of the amorphized surface layer of our Si samples. At annealing temperatures above 500 °C the segregation of the Co to the surface is clearly observed.

Implantation dose.—The relative intensity of the quadrupole doublet compared to the total spectrum area was found to be inversely proportional to the Co concentration. It is barely visible at doses above 10^{14} atoms/cm^2 but becomes more and more intense for lower implantation doses and dominates the Mössbauer spectrum at 2.5×10^{12} atoms/cm^2 as shown in Fig. 1.

Si dopant.—Also, a strong Si-dopant dependence was observed when we compared float-zone Si targets (Wacker Chemitronic) doped with B or P with local dopant concentrations in the range of 10^{17}–10^{18} atoms/cm^3 (resistivity 0.06–0.13 Ω cm). The local average Co concentration in the implanted region varies between 10^{17} and 10^{19} atoms/cm^3 for the implantation doses between 10^{12} and 10^{14} atoms/cm^2 used in the present study. In B-doped Si the side peaks of this quadrupole doublet were al-

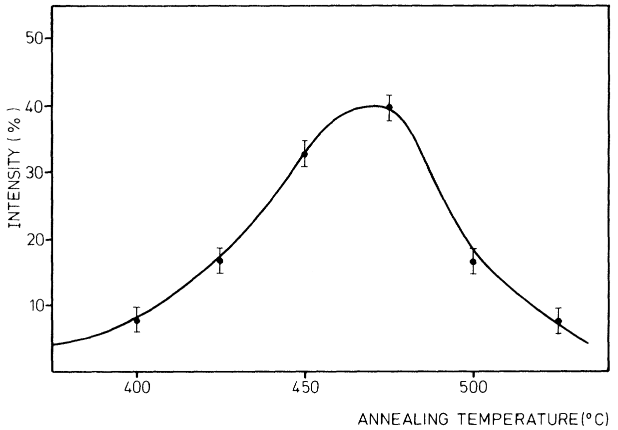

FIG. 2. Relative intensity of the outer quadrupole doublet as a function of annealing temperature using a 5×10^{12}-atoms/cm^2 source of ^{57}Co implanted into *n*-type Si.

ways only very weakly present.

Measuring temperature.—A Si target implanted with ^{57}Co to 2.5×10^{12} atoms/cm^2 was annealed to 475 °C in order to obtain a maximum intensity of this spectrum component. We then measured the Mössbauer spectrum for different temperatures between 4 and 300 K, while the absorber was kept at 78 K. The spectra are shown in Fig. 3. Each of these spectra took about 10 d measuring time, with use of two superimposed Si wafers implanted on both sides. A very clear temperature dependence can be observed for the two lines of the quadrupole doublet. When lowering the temperature below room temperature the doublet becomes more and more asymmetric, while the positive-velocity resonance broadens much faster than the other one. Below 78 K this tendency reverses, and the symmetry is almost completely restored at 4 K. Apart from the second-order Doppler shift the velocity position of all spectrum components remains the same. Moreover, a fit of the spectrum shows that the area of both resonances of the quadrupole doublet remains constant throughout the whole temperature range, so that the origin of the asymmetry is an asymmetric broadening.

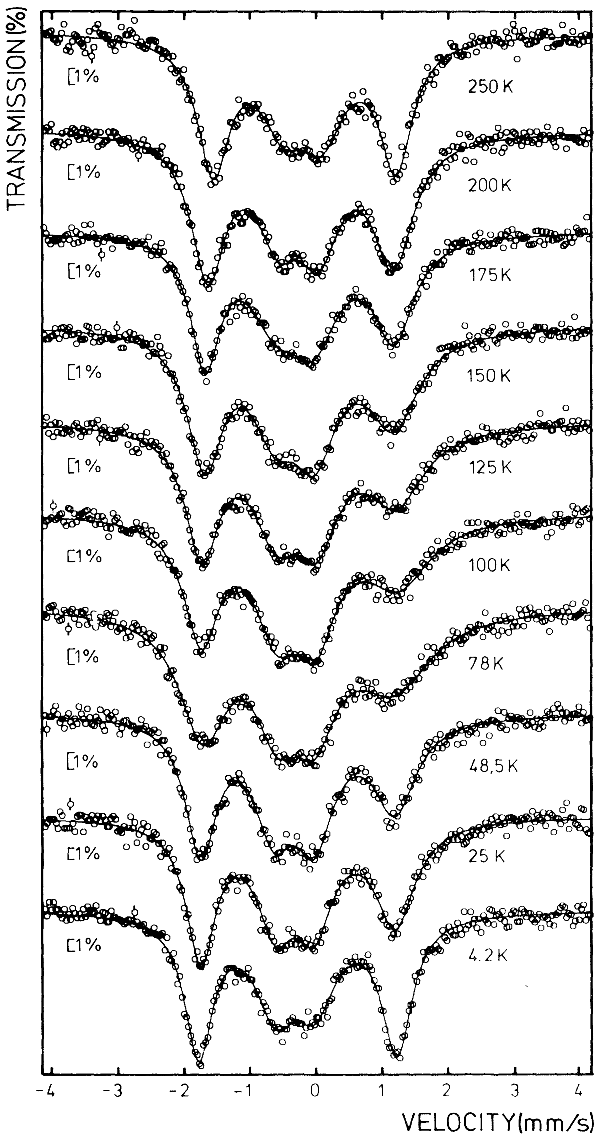

FIG. 3. Mössbauer spectra as a function of measuring temperature using a 2.5×10^{12}-atoms/cm^2 source of ^{57}Co implanted into *n*-type Si.

On the basis of the observed dependence on annealing temperature, implantation dose, Si doping, and measuring temperature, we associate this quadrupole doublet with the formation of Co dimers.

The Mössbauer parameters are not unrealistic for such an assumption. As we measure in fact ^{57}Fe Mössbauer spectra, the observed Mössbauer parameters belong to a ^{57}FeCo molecule, formed only nanoseconds before the measurement, by the radioactive decay of one of the dimer constituents. Isolated ^{57}FeCo molecules were studied by Mössbauer spectroscopy in matrix isolation experiments in frozen argon by Montano and a QS of 3.60(5) mm/s and IS of +0.55(5) mm/s were measured.[11] A smaller QS is indeed expected when the dimeric molecule is incorporated in a matrix where the host atom participation in the bonding tends to reduce the asymmetry of the bonding orbitals. The IS has shifted towards a higher *s*-electron density in Si, which might be indicative for a smaller available volume for the molecule, but the observed electron density is the global effect of changes in direct *s*-electron density and in indirect *d*-electron shielding, in which the bonding to the Si atoms also plays a role.

The coincidence of the annealing temperature at which this doublet appears with the recrystallization temperature of Si certainly supports a picture in which the Co atoms start to diffuse and in a first stage of precipitation start to form dimers. Also in the already mentioned matrix isolation experiments[11] the formation of transition-metal dimers was readily observed. For higher annealing temperatures larger clusters are formed which are expected to have smaller quadrupole splittings, and therefore cannot be distinguished from the Co silicides in the central part of the spectrum. If the proposed scenario holds, then the fraction of Co dimers as a function of increasing Co concentration first should increase when the solubility limit is exceeded, while at higher concentrations, this fraction should decrease again as larger clusters are formed more readily. Our experiments are consistent with such a decrease.

Also a dopant dependence is expected because of the known tendency of acceptor-type dopants to form pairs with diffusing transition-metal impurities. The diffusing Co atoms are indeed attracted by the acceptor-type dopants, but the annealing temperature is already so high that the formed Co-B pairs are not stable any more.[12] In this case the acceptor-type atoms act merely as a catalyst for the formation of larger Co clusters, and their presence initiates a competing mechanism at the cost of Co-dimer formation.

One of the most convincing arguments for the association of the quadrupole doublet with Co dimers is the observed asymmetric broadening in the spectrum. Such a behavior is typically induced by fluctuating magnetic fields as a result of electronic relaxation effects, as discussed by Blume.[13] A spin-lattice relaxation which is slowing down for decreasing temperatures can explain the increasing asymmetric broadening between 300 and 78 K. This relaxation process takes place between the magnetic energy levels of the dimeric molecule. The spacing between these levels depends on the exchange interaction strength between the two atoms. In Mössbauer studies[14] of Fe dimers which were part of larger organic molecules this exchange interaction was observed to be of the order of several inverse centimeters, so that at low enough temperatures only the lowest state is occupied. In these studies the coupling between the two dimer constituents was antiferromagnetic so that no magnetic moment is carried in the lowest state, and because of this a symmetric quadrupole doublet was observed at low enough temperatures. Our data below 78 K can be accounted for by similar arguments: a gradual depopulation of higher-lying magnetic levels in favor of a nonmagnetic ground state of the FeCo molecule, and an electronic relaxation time of the order of magnitude of the nuclear Larmor precession time. A quantitative analysis of the parameters that govern the observed relaxation effects is not very meaningful here as the involved parameters, e.g., the exchange interaction strength and the thermal variation of the relaxation rate, are strongly correlated.

We feel that all of this evidence points towards Co dimers, and in this way our study is the first report on a well-defined defect configuration in Si involving only Co atoms. Although the formation of some Fe-Co pairs during the annealing step is not excluded because of the presence of some ^{57}Fe from the implanted beam (about 10%), and from implanted ^{57}Co nuclei that have decayed ($T_{1/2} = 271$ d), no extra components could be observed within the statistical accuracy of the Mössbauer spectrum. This is probably mainly due to the fact that we always studied freshly implanted samples, but might also indicate a preferential tendency to form pure dimers.

We feel that our results on Co dimers are indicative of the kind of defects that are formed by easily precipitating transition metals in Si. The importance of this type of defect can be judged by the fact that at the lowest concentrations studied almost all of the Co atoms were involved in the formation of Co dimers. Moreover, the striking dopant dependence observed is important for the role of such defects in the performance of Si-based devices. Finally, the results of this study also shed some light on the mechanism of silicide formation, which clearly starts by a nucleation by Co dimers.

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