Far-infrared spectroscopic, magnetotransport, and x-ray study of athermal annealing in neutron-transmutation-doped silicon

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We present evidence that the energy introduced by a short laser pulse focused to high intensity on a small spot on the surface of neutron-transmutation-doped silicon electrically activates impurities far away from the focal spot. The activation of the impurities is measured by far-infrared spectroscopy of shallow donor levels and by magnetotransport characterization. Electrical activity is comparable to that obtained with conventional thermal annealing. X-ray rocking curve measurements show strain in the area of the focal spot, but none at large distances from the focal spot. © *1997 American Institute of Physics.* [S0003-6951(97)04531-2]

We provide evidence for a new semiconductor annealing method that is athermal in nature[1] and which, because it is faster, may be accompanied by far less diffusion than conventional thermal annealing techniques. Energy introduced by a laser pulse focused to high intensity on a small spot on the surface of neutron-transmutation-doped (NTD) silicon electrically activates the phosphorus donors at distances as far as 12.5 mm from the focal spot. The best obtained electrical characteristics of athermally annealed (AA) samples, as determined by far-infrared absorption and magnetotransport, are comparable to the best attained with conventional furnace annealing.

Seven $25\times25\times2$ mm Si samples were cut from a boule of high-purity, float-zone (FZ) Si from Wacker Chemical. The boule was oriented along the (111) direction. The samples were then neutron-transmutation doped[2] by exposure to a thermal neutron flux of 1.2×10^{13} cm^{-2} s^{-1} for 110 h. The P concentration produced in these samples was about 10^{15} cm^{-3}. The samples were then irradiated under vacuum by one or two pulses from the PHAROS III laser at the Naval Research Laboratory ($\lambda=1.06\ \mu$m, $t=5$ ns, $E\sim10$ J) focused to a spot 1 mm in diameter on the surface of the sample. Two of the seven irradiated samples showed dopant activation comparable to that seen in thermally annealed control samples. The experimental results for those two samples are discussed below.

The electrical activity of the impurities was measured by far-infrared absorption. It is known that both shallow donors and shallow acceptors in semiconductors, including Si, create energy levels analogous to those in a hydrogen atom.[3] In addition, the integrated intensities of the Lyman lines are directly proportional to the concentration of electrically active donors in the sample. Because the electron binding energy for P is only $\sim$44 meV below the conduction band of Si, its Lyman spectrum occurs in the far infrared (250–400 cm^{-1}).

To determine the P activation in the samples, infrared spectra were obtained using a Bomem DA3.01 Fourier transform spectrometer at a spectral resolution of 0.1 cm^{-1}. During data acquisition, the samples were cooled to a temperature of 5.5 K using a continuous flow liquid-helium cryostat. In addition to the athermally treated samples, measurements were made on three other control samples: an as-grown sample, an unannealed NTD sample, and a thermally annealed NTD sample. The results for the control samples and the two AA samples, labeled AA-1 and AA-2 that showed evidence of annealing are presented below.

The frequency dependence of the absorption coefficient of the as-grown sample is shown in Fig. 1(a). The spectrum is flat except for two peaks that are Lyman lines 2 and 4 of boron[4] present in the as-grown material at a concentration of 8.8×10^{13} cm^{-3}. After neutron irradiation, the frequency dependence of the absorption coefficient is completely flat [Fig. 1(b)]. The absence of any Lyman lines due either to boron or phosphorus indicates the absence of electrically active donors or acceptors.

The frequency dependence of the absorption coefficient for a NTD sample after annealing at 900 °C for 1 h in a nitrogen atmosphere is shown in Fig. 1(c). Five phosphorus Lyman lines are now visible.[5] The boron acceptor lines from Fig. 1(a) are absent because the acceptors in the annealed NTD *n*-type sample are all ionized.[5]

Figure 2 shows the absorption spectra for two samples that were irradiated by the laser. Note that a large number of Lyman lines are visible in both cases, in fact, more than in the thermally processed sample. This is probably due to a higher level of strain in the thermally processed sample, since all samples had approximately the same phosphorus concentration. The frequencies of the lines agree well with previous measurements.[5] Transition assignments are labeled in Fig. 2(a).

We can assess the degree of activation of the phosphorus dopants in the thermally annealed and athermally annealed samples by comparing the integrated areas of the $2p_\pm$ peaks after fitting with a Lorentzian and estimating the active donor concentration using published calibration factors.[6] The integrated area under the $2p_\pm$ line at 316 cm^{-1} is 15.4 ±1.0 cm^{-2} for the two athermally annealed samples, and

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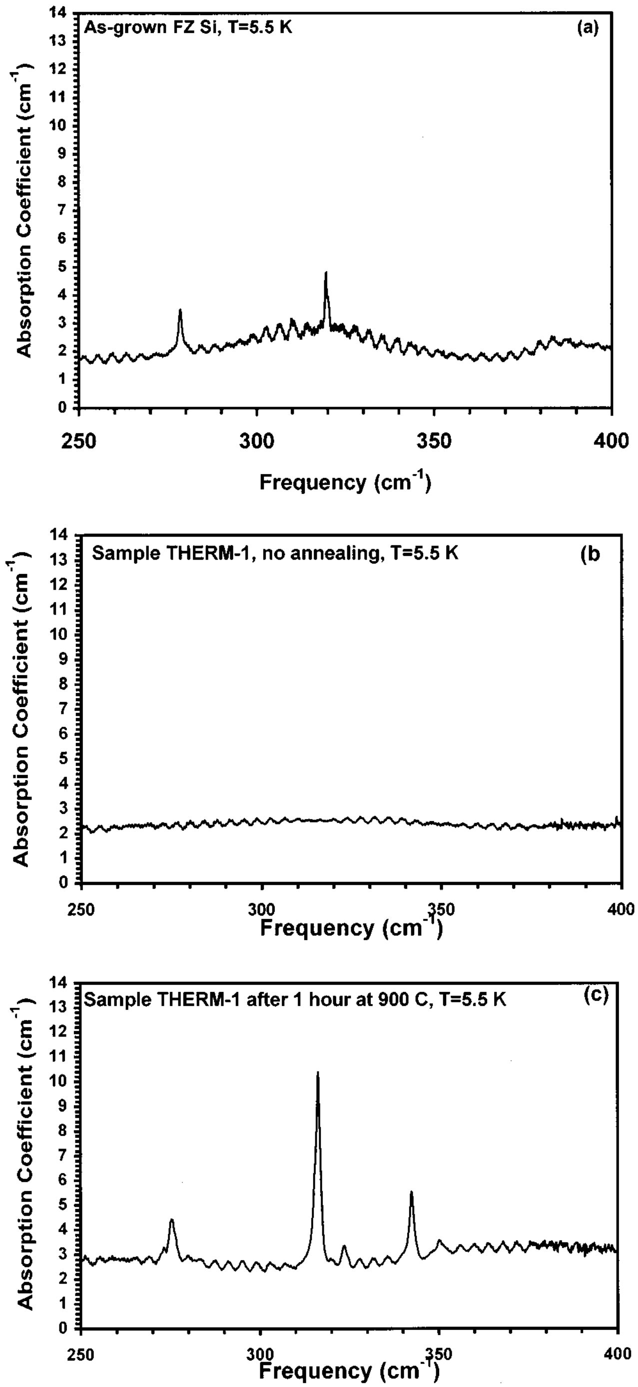

FIG. 1. Absorption coefficient as a function of frequency for (a) an as-grown FZ silicon sample. (b) FZ silicon sample THERM-1 after exposure to a thermal neutron flux of $1.2\times10^{13}\,cm^{-2}\,s^{-1}$ for 110 h. (c) Sample THERM-1 after annealing for 1 h at 900 °C in a nitrogen atmosphere. Data obtained at 5.5 K.

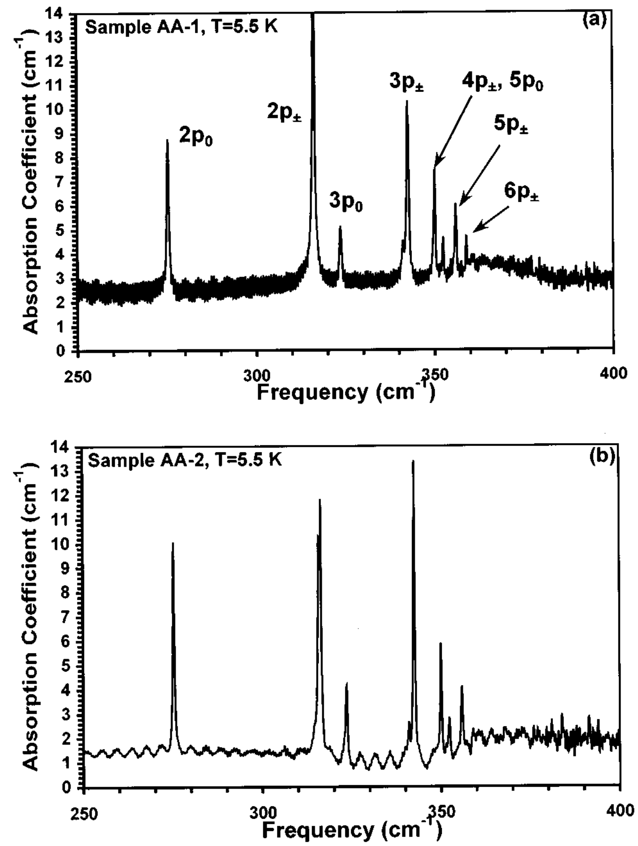

FIG. 2. Absorption coefficient as a function of frequency of samples (a) AA-1 and (b) AA-2. Both samples were subjected to a 10 J laser pulse focused to a 1 mm spot on the sample. Data obtained at 5.5 K.

$18.5\pm0.5\,cm^{-2}$ for the thermally annealed sample. Using a calibration factor of $4.28\times10^{13}\,cm^{-1}$,[6] we obtain activated donor concentrations of $6.6\pm0.4\times10^{14}$ and $7.9\pm0.2\times10^{14}\,cm^{-3}$ for the athermally and thermally annealed cases, respectively. Because calibration factors are very sample dependent,[6] these numbers are only estimates. Nevertheless, they agree well with the nominal concentrations of impurities, and with the magnetotransport results discussed below.

Samples AA-1 and AA-2 were also characterized electrically, along with control samples. Following the evaporation and sintering of Al contacts at the four corners using a low-temperature process, the Van der Pauw method was employed to determine the resistivities and Hall coefficients at magnetic fields between 0 and 7 T and at temperatures between 20 and 300 K.

A sample that had not been neutron irradiated was found to be p type with a net acceptor concentration of $9\times10^{14}\,cm^{-3}$. Two other samples that were neutron irradiated, but not annealed by either method, had unmeasurably high resistances (at least three orders of magnitude higher than in any of the annealed samples) as determined by four-point probe measurements. Field dependent magnetotransport measurements on the thermally annealed NTD sample indicated normal n-type conduction at temperatures near ambient, with a net electron concentration of $3.1\times10^{14}\,cm^{-3}$ and mobility of $1570\,cm^2/V\,s$ at 300 K.

The Van der Pauw characterization was performed on samples AA-1 and AA-2 following the athermal annealing. Analysis by the quantitative mobility spectrum analysis technique[7] confirmed that apart from a recognizable signature due to the Hall factor and mass anisotropy, only a single electron species was present. The electron densities represented by the filled points in Fig. 3 confirm that the AA process induced activation of $\approx1.1\times10^{15}\,cm^{-3}$ donors in both samples. A fit to the standard freeze-out relation[8] in the absence of compensation (curve) implies a binding energy of 43 meV. This agrees well with previous results for Si:P.[9,10] The mobilities given by the filled points in Fig. 4 also agree

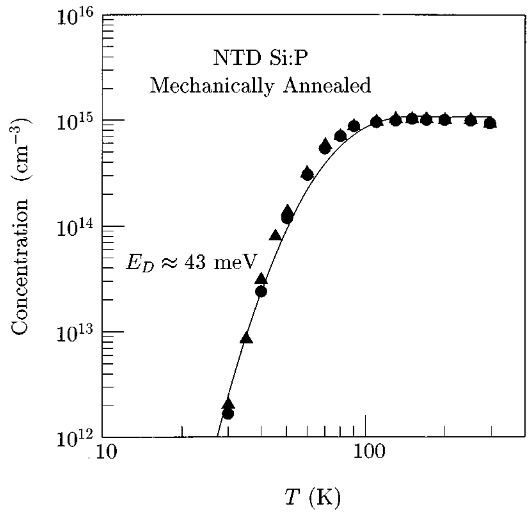

FIG. 3. Electron concentration vs temperature for mechanical-energy-annealed samples AA-1 (filled circles) and AA-2 (filled triangles). The curve represents a fit to the low-temperature freeze-out, which implies a donor binding energy of 43 meV.

with the expected dependence, as may be seen by comparing with the open boxes corresponding to a melt-grown Si:P sample with $N_D = 9.6\times10^{14}$ cm^{-3} and $N_A = 2.0\times10^{14}$ cm^{-3}.[10] The slightly higher mobilities in the AA samples at $T \leqslant 40$ K probably indicate a somewhat lower compensation.

Taken together, these results imply that the athermal annealing of the two samples produced both excellent donor activation with little compensation, and healing of the neutron-induced damage to the extent that the carrier mobility, $\mu_n(T)$, approaches its theoretical limit.[11] Four-point probe measurements with 2.25 mm spatial resolution on the two AA samples yielded a uniform sheet resistivity of 56 ±1 Ω/square everywhere on the sample's front and back surfaces, indicating that the laser irradiation focused in the center produced uniform n-type activation over the entire 25 mm square samples.

In an attempt to assess the degree of structural repair, x-ray diffraction studies were carried out on the four samples. Both lattice parameters and rocking curves were measured on a four-circle diffractometer using a technique described elsewhere.[12–14]

Rocking curve widths and lattice parameters for both an as-grown sample and a sample that had been neutron irradiated but not annealed gave identical results, a lattice constant of 5.4300 Å and a rocking curve width of 24 arcsec. This is due to the fact that the x-ray diffraction technique is not sensitive to the type of damage, primarily point defects, caused by neutron irradiation. Lattice constant measurements on the AA samples will also allow us to determine if the AA technique introduces any additional large-scale damage in the Si. Lattice constants within 2 mm of the focal spot on the AA samples have values ranging from 5.4221 to 5.4387 Å, indicating the presence of compressive and tensile strain in a 1–2 mm diam region around the focal spot. Lattice parameters further from the focal spot are identical to that of the as-grown sample demonstrating that in the large majority of the sample no strain is induced by the AA technique.

In conclusion, we have demonstrated that phosphorus impurities in neutron-transmutation-doped silicon can be electrically activated without bulk heating. A short laser pulse focused to high intensity on a small spot on a NTD sample can anneal areas of the sample far outside the laser spot. The features in the infrared spectra of the laser processed samples were sharper than those in similar thermally processed samples, possibly indicating lower strain in the laser processed samples. Active donor concentrations were comparable in both processes, but the athermal process was accomplished in a much shorter time than bulk heating. Because of the short time scale involved in the athermal process, it is expected to involve much less diffusion of dopants than thermal processes.

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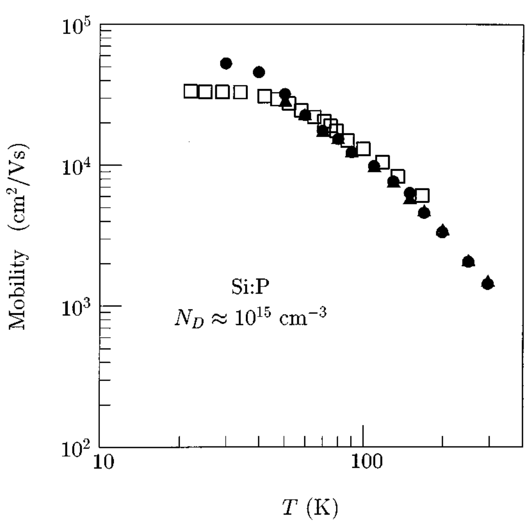

FIG. 4. Electron mobility vs temperature for the same two AA samples (filled points). Also shown for comparison is the analogous dependence for a melt-grown Si:P sample (open boxes) with comparable net donor concentration (Ref. 10) (curve).

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