APPLIED PHYSICS LETTERS VOLUME 77, NUMBER 13 25 SEPTEMBER 2000

Athermal annealing of phosphorus-ion-implanted silicon

J. Grun[a] and R. P. Fischer
Plasma Physics Division, Naval Research Laboratory, Washington, DC 20375

M. Peckerar
Electronic Science and Technology Division, Naval Research Laboratory, Washington, DC 20375

C. L. Felix
Unified Industries Inc., Springfield VA 22150

B. C. Covington
Southwest Texas State University, San Marcos, Texas 78666

W. J. DeSisto
Electronic Science and Technology Division, Naval Research Laboratory, Washington, DC 20375

D. W. Donnelly
Department of Physics, Sam Houston State University, Huntsville, Texas 77341

A. Ting
Plasma Physics Division, Naval Research Laboratory, Washington, DC 20375

C. K. Manka
Research Support Instruments, Lanham, Maryland 20706

(Received 5 June 2000; accepted for publication 31 July 2000)

A 1 cm^2 area in phosphorus-implanted silicon samples is annealed by irradiation of a much smaller 0.002 cm^2 area with a single laser pulse. Resistivity of the annealed region is uniform and similar to that measured after thermal annealing. Electrically activated donors did not diffuse into the sample and only slightly towards the sample surface. The process is 100% reproducible. We present evidence that the annealing is not caused by heat.

We show that a single laser pulse focused to a 0.002 cm^2 spot, activates donors within a surrounding 1 cm^2 region of silicon samples ion implanted with phosphorus at a concentration of 10^{20} ions/cm^3. For convenience, and since no heat is deposited in the activated region we call the process athermal annealing (AA). Resistivity within the AA region is uniform and similar to what can be achieved with thermal annealing. But, AA produces virtually no diffusion of phosphorus donors into the sample and only a little toward the sample surface. Unlike previous reports on AA of neutron-transmutation-doped silicon,[1,2] results here are obtained on 100% of the AA'd samples.

The experiments are performed on 10-cm-diam, 1/2-mm-thick p-type silicon wafers with sheet resistance of several thousand Ω cm, implanted at 100–110 keV to an areal density of $\sim 10^{17}$ phosphorus ions/cm^2. The resistivities of the samples after implantation are 2500 and ~ 50 $\Omega/\square$ after thermal annealing at 900 °C in nitrogen for 1 h. These wafers are placed in a vacuum chamber and irradiated within a $\sim 1/2$ mm diam spot by a 0–30 J, 5–40 ns duration, 1.06 μm wavelength laser pulse. Typical intensity within the spot is 10^{12}–10^{13} W/cm^2, which is sufficiently high to produce hot plasma that streams away from the irradiated spot at high velocity, thereby launching multimode acoustical stress waves and shock waves into the wafer.[3] About 2.5 cm beneath the wafer is an adjustable radiant-heat source capable of raising the wafer to a temperature of up to 600 °C (measured with a thermocouple). As-implanted and thermally annealed samples are used as controls.

Figure 1(a) is an image of the implanted, laser-irradiated side of a typical sample. The most prominent feature in this

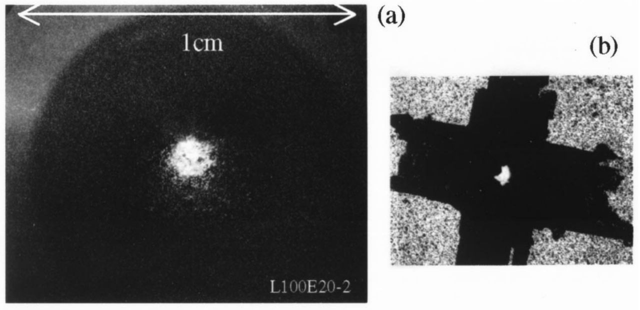

FIG. 1. Images of a phosphorus-implanted sample after laser irradiation: (a) The implanted, laser-irradiated side of the sample shows a disk-shaped AA region with a small ($\sim$1 mm) crater at its center. (b) The unimplanted side opposite the crater shows evidence of spallation which manifests itself as small hole and a ''+'' shape within which silicon has been removed. The ''+'' is aligned along the silicon crystal axes. These images are typical. There are no discernible differences between images of samples irradiated at room temperatures or at higher temperatures <600 °C.

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[a] Author to whom correspondence should be addressed; electronic mail: grun@nrl.navy.mil

image is a bright, $\sim$1-mm-diam spot, which is the crater formed by pressure from the hot plasma produced by our high-intensity laser pulse. Surrounding the crater is a disk with coloration similar to nonimplanted silicon and darker than the rest of the implanted sample. This is the AA'd region. Its coloration is the result of recrystallization of the implant. Note the abrupt change from the AA'd to unannealed state at the edge of the disk, perhaps indicating a threshold effect in the annealing process. Figure 1(b), an image of the unirradiated side of the wafer, shows a "+" like feature surrounding a small bright spot. This is spallation caused by shocks from the laser-irradiated spot.

Resistivity in the AA'd region, measured on different samples with a four-point probe (1.5 mm resolution) and a current–voltage probe (≤ 0.1 mm resolution) varies from 60 to 140 $\Omega/\square$, which is much lower than the 2500 $\Omega/\square$ resistivity of an implanted control. Within individual AA'd regions the resistivity is constant to within the accuracy of the measurement and drops precipitously at the regions edge. Resistivity of the AA'd region is independent of sample temperature, laser energy, and small variations in laser pulse duration (Fig. 2). However, the AA'd region's diameter does grow with increasing laser energy up to about 15 J, where further growth ceases. This cessation of growth correlates with the appearance of a hole, with dimensions comparable to the laser spot, punched through the wafer. The diameter of the largest AA'd region is 1.1 cm.

Infrared absorption measurements show that the number of donors activated by AA is comparable to the number of donors activated within thermally annealed controls. The degree of activation is determined by integrating the absorption coefficients of infrared light from 150 to 400 cm^{-1} in samples cooled to 5.2 K in order to minimize absorption by vibrational modes.[4] Within the AA'd region the integral is 5215 ± 181 cm^{-2}, which is comparable to 4777 ± 138 cm^{-2} for a thermally annealed control, while the integral in an as-implanted sample is a significantly lower 1121 ± 164 cm^{-2}. Far from the AA region infrared absorption is 1287 ± 57 cm^{-2}, indicating little or no activation there. This is so even in samples preheated to 400 °C prior to laser irradiation, where a reduction in four-point probe resistivity was measured [see Fig. 2(b)].

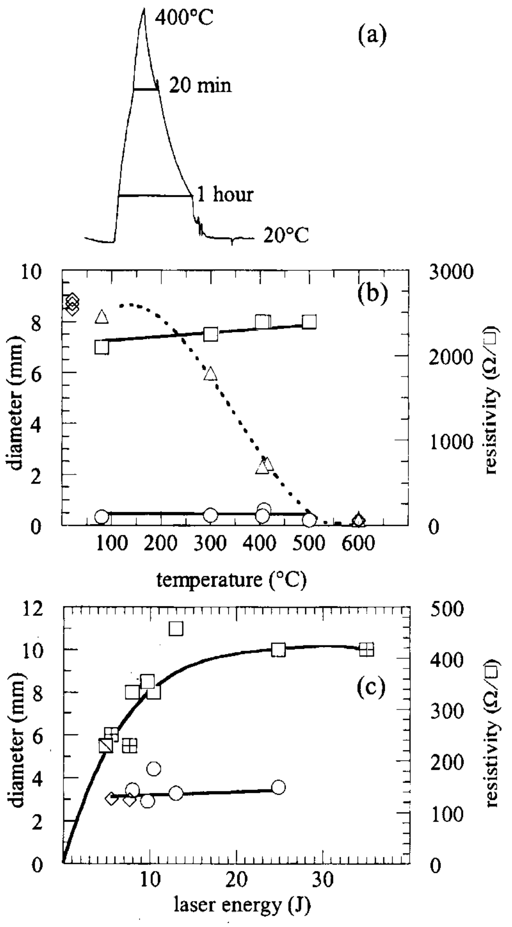

FIG. 2. Size and resistivity of the phosphorus-implanted, AA region as a function of sample temperature, laser energy, and laser pulse duration. (a) Typical sample-temperature profile. Heater current is increased until the sample temperature rises to a desired peak temperature. The laser is discharged at peak temperature and the current to the heater is turned off so the sample can cool. Kinks in the profile reflect heater current adjustments, filling the vacuum chamber with air and the like. (b) Dependence on peak sample temperature at a fixed laser energy of 10 J and a pulse duration at 10 ns. (□) and (○) represent the diameter and resistivity of the AA region; (△) represents the resistivity of the sample outside the AA region; and (◇) is the resistivity of a heated but unirradiated reference sample. The AA region shows no dependence on peak temperature. Note that the resistivity of the sample outside the AA region decreases with peak temperature even though the sample is heated for a relative short time. (c) Dependence on laser energy and pulse duration. (□) represent AA diameters at 10 ns, 400 °C (plain); 35 ns, 20 °C (crossed); and 10 ns, 20 °C (back slashed). (○), (◇) represent AA resistivity at 10 ns, 400 °C and 35 ns, 20 °C, respectively. The AA region diameter increases with energy until spall limits the mechanical energy available for AA. (Amount of spall is estimated from a visual examination of the sample.)

Donor diffusion in the AA'd region, measured here in samples irradiated at room temperature only, is minimal.[5] Figure 3 compares the concentration of phosphorus donors as a function of depth at three locations: at the crater edge where rapid melting and resolidification occur, inside the AA'd region, and outside the AA'd region where the sample conditions are "as implanted." Notice that the donor distribution in the AA'd region does not show any diffusion into the sample: To the right of the concentration peak (i.e., in the direction away from the surface) the as-implanted and AA'd distributions are indistinguishable. To the left of the peak (nearer the surface), AA'd donors at concentrations below 2×10^{19} ions/cm^3 tend to move closer to the surface by about 400 Å. This is unlike what occurs in thermal annealing processes where diffusion exists on either side of the distribution peak. Here too, near the heated crater edge, diffusion of about 300–400 Å into the sample and towards its surface is seen. In all three cases the distributions merge at concentrations of $\sim10^{18}$ ions/cm^3.

Although the AA'd region has uniform resistivity, Raman backscatter measurements (resolution of 0.2 mm) imply variations in its crystal structure. For instance, near the edge of the crater, Raman backscattered light displays a peak at 521 cm^{-1}, with a width of 7.3 cm^{-1}, and a relative amplitude of 19 000 counts. (Raman from crystalline silicon exhibits a peak at 521 cm^{-1} with a width of 7 cm^{-1}.) Away from the crater the Raman signal is reduced in amplitude and its peak shifts to shorter wave numbers until, just within the edge of the AA'd region, the peak is at 519 cm^{-1}, the signal has a width of 7.0 cm^{-1}, and the relative amplitude is 600 counts. Outside the AA'd region the Raman backscatter peak

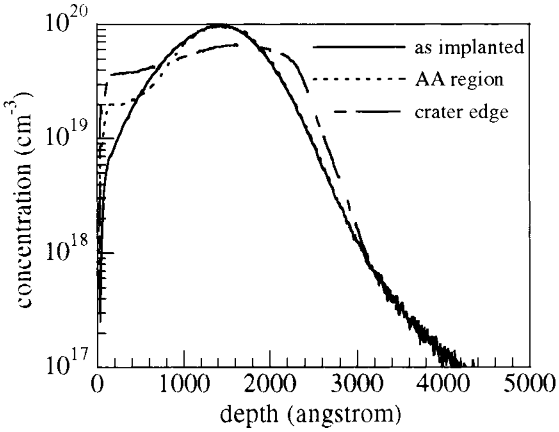

FIG. 3. Concentration of phosphorus ions as a function of depth for as-implanted (solid line) and AA samples (dotted line) irradiated at room temperature. The dashed line indicates a measurement near the crater edge, where melting and resolidification occur. The measurements were performed with a SIMS.

is at 470 cm^{-1}, its width is 100 cm^{-1}, and its amplitude is 100 counts. This indicates[6] that crystalline islands near the edge of the crater structure are largest (>30 Å), that they become smaller with distance from the crater (~30 Å near the edge of the AA'd disk), and that their size is negligible outside the AA'd disk where the implant is amorphous. Electron microscope, and *x*-ray topography images of the AA region show evidence of the region having been stressed.

A plausible explanation for AA is that acoustical stress waves and shock waves generated by plasma within the focal spot provide the energy for annealing. Evidence of the AA region having been stressed and the cessation of AA region growth once a hole is punched through the wafer provide indirect support for this explanation. Other sources of energy such as radiation from the focal-spot plasma, scattered infrared laser light, redeposition of doped silicon plasma on the surface of the wafer, heat conduction from the focal spot, or thermal energy released through recrystallization, are inconsistent with observations. For example, when the laser illuminates a surrogate piece of silicon placed a fraction of a millimeter above a doped sample no annealing of the doped sample occurs, even though it is exposed to virtually the same radiation as when the laser illuminates it directly. This eliminates radiation from the focal-spot plasma and scattered laser light from consideration. A sample coated with a thin layer of photoresist coating and illuminated by a laser pulse is annealed underneath the coating, eliminating redeposited plasma effects as an explanation.

To eliminate heat conduction we performed tests utilizing a ''temperature diagnostic,'' which consisted of an array of rectangular lines, 0.3 μm tall, 0.5 μm wide, and separated by 0.5 mm of photoresist[7] coated on a silicon wafer. Melting causes the resist to flow, decreasing the height of the lines and broadening their width, thereby providing detectable verification of the resist having exceeded its melt temperature. Heating in an oven at 200 °C for 1/2 h decreased the height of the lines by 1/3. Rapid heating of the resist near the focal spot of the laser produced discoloration easily seen by the eye and a rounding of the pattern edges visible with an electron microscope.

The tests consisted of two parts. First, we showed that temperatures capable of melting the resist were insufficient to anneal. Second, we produced annealing at temperatures too low for the resist to melt. The combination implies that a mechanism other than heat produced the annealing. In the first part, a surrogate piece of silicon was placed a fraction of a millimeter above an ion-doped sample and irradiated with a typical laser pulse. Plasma radiation from the surrogate illuminated the doped sample, but heat from the focal spot could not diffuse into the doped sample since it was separated from the surrogate by vacuum. Under these circumstances the doped sample did not anneal. When the test was repeated with our temperature diagnostic in place of the doped sample, the resist lines disappeared. Thus, a temperature that melted the diagnostic resist was not high enough to anneal. In the second part, the doped sample was illuminated as is usual in these experiments, but it was protected from plasma radiation by a shield (brass sheet or another thin sheet of silicon). When this was done the doped sample annealed. When the doped sample was replaced by the temperature diagnostic the lines did not change, indicating that heat diffusion does not raise the surface temperature above that needed for resist melting. Furthermore, since athermal annealing itself does not melt the temperature diagnostic, any heat liberated in the process of recrystallization is eliminated as a possible cause of AA.

In conclusion, we demonstrated a process that electrically activates phosphorus-ion-implanted silicon without significant heating of the annealed region. Electrically activated donors were shown not to diffuse into the sample and only slightly towards the sample surface. Reproducibility was excellent. We provided direct evidence that AA is not caused by heat and indirect evidence that it is caused by mechanical energy.

The authors thank R. Burris and Dr. S. Jackel for building their laser, Dr. Larry Larson for advice and encouragement, Dr. O. Glembocki for the Raman measurements, Dr. M. Fatemi for the x-ray topography measurements, Joe Bennett for the secondary ion mass spectrometry (SIMS) measurement, and the NRL NPF for preparing certain samples. This work is supported by The Office of Naval Research. Dr. Donnelly is supported by the National Science Foundation.

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