

Annealing of phosphorus-ion-implanted silicon using a CO₂ laser

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silicides in the Ni and Pt systems. When the metal is completely consumed in the formation of Ni_2Si and Pt_2Si , subsequent bombardment does not lead to the formation of the monosilicide, but rather to the formation of an amorphous Si-enriched structure. In the case of the Pt system, thermal annealing of the ion-mixed amorphous layers at temperatures of 400–500 °C can lead to formation of PtSi or the metastable phase Pt_2Si_3 , depending upon the amount of Si enrichment produced by the ion beam.¹⁴ We attribute the difference in behavior between the Pd system and the Pt and Ni systems to the stability of PdSi under ion bombardment. This is evidenced by the experimental observation that irradiation of samples of PdSi and PtSi with 2×10^{15} Xe ions/cm² at an energy of 300 keV resulted in the disappearance of the x-ray-diffraction lines of PtSi, but only to a weakening of the PdSi lines.

In summary, we have demonstrated that the penetration of ions through the Pd_2Si -Si interface leads to the formation of PdSi. In addition, once the PdSi phase is formed, further growth of PdSi can be achieved by postannealing at temperatures around 350 °C. This result suggests that it is the stability of the Pd_2Si -Si interface that prevents the formation of PdSi at such temperatures. The penetration of energetic ions through the interface leads to the formation of PdSi which can then grow with further bombardment or postannealing. The results also indicate that the resistance of the structure under ion irradiation determines whether a silicide is formed (Pd/Si system) or a mixed metal-Si amor-

phous structure (Pt/Si system) is formed. In the latter case, a silicide structure can be recovered by postannealing.¹⁴

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Annealing of phosphorus-ion-implanted silicon using a CO₂ laser

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Annealing behavior of phosphorus implanted in silicon layers under cw CO₂ laser irradiation is investigated. The irradiation time required for full electrical activation is found to depend on the dopant concentration of the substrate. This is because absorption of CO₂ laser light is a function of free-carrier concentration in the crystalline substrate. During the experiment, an enhancement of annealing efficiency is observed in the case of a low-resistivity substrate or with bias light (Xe lamp) irradiation. This supports the above explanation.

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Recent experiments have shown that irradiation with high-power ruby,^{1,2} Nd : YAG,^{3,4} and cw argon⁵ lasers appears to be an effective substitute for furnace annealing of ion-implanted silicon. However, penetration of these laser light beams into ion-implanted silicon is limited to a shallow region only a few μm from the surface. When deep annealing is necessary, lasers with infrared wavelength must be used.

Thus, our experiment undertook to investigate the possible annealing behavior of ion-implanted silicon under CO₂ laser (10.6- μm wavelength) irradiation.

Silicon *p*-type (100) wafers with different dopant concentrations (1.4×10^{14} to $1.5 \times 10^{16} \text{ cm}^{-3}$) were used. Phosphorus ions were implanted at 50 keV with a dose of $5 \times 10^{15} \text{ cm}^{-2}$. A cw CO₂ laser, with an output of 50 W and spot size 0.65 mm in diameter, was utilized. Laser light was irradiated into the specimen in the dark or under uv light excitation from a Xe lamp (supplied voltage: 100 V; current: 5 A). Carrier concentrations and mobilities in the implanted and laser-irradiated layers were determined by van der Paw's method.⁶ The imaginary part of the optical constant was

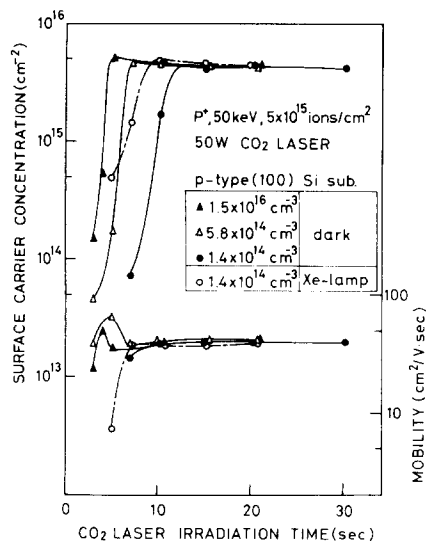


FIG. 1. Surface carrier concentration and electron mobilities after laser irradiation for samples with different substrate doping density. Laser light was irradiated into specimen in the dark ($\blacktriangle, \triangle, \bullet$) or under uv light excitation (\circ).

measured by ellipsometry.⁷ Optical reflection⁸ at 2750 Å was also measured to determine the degree of substrate damage. Carrier and damage profiles were determined through sheet resistivity (using Irvin's data⁹) and optical reflection measurements combined with a conventional anodic oxidation layer removal method.

Surface carrier concentration and electron mobilities after laser irradiation are shown in Fig. 1 as a function of irradiation time. Surface carrier concentration first increased rapidly with the increase in laser irradiation. It saturated to $5 \times 10^{15} \text{ cm}^{-2}$ after from 3 to 10 sec. Thus, nearly 100% electrical activation was obtained by the irradiation. The irradiation time necessary to obtain full electrical activation was dependent on substrate dopant concentration,

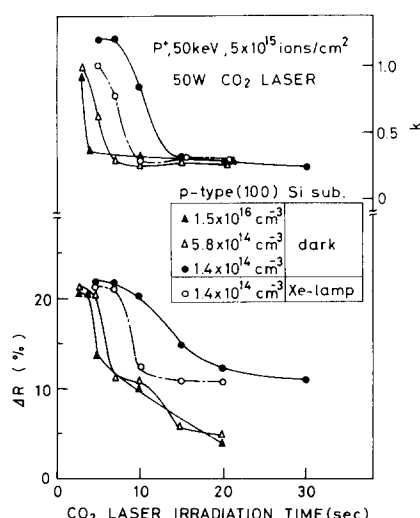


FIG. 2. Imaginary part of optical constant k and optical reflectivity change (ΔR) after laser irradiation for samples with different substrate doping density. Laser light was irradiated into specimen in the dark ($\blacktriangle, \triangle, \bullet$) or under uv light excitation (\circ).

the lower the concentration the longer the irradiation time required.

The electron mobilities increased as the laser irradiation time was increased from 3 to 5 sec. However, a further increase in irradiation time resulted in a decrease of electron mobility (Fig. 1). Consequently, the damaged layer was assumed to have returned to the crystalline state between 3 and 5 sec. After this operation, electron mobilities were governed by the impurity scattering mechanism in the crystalline state.

The imaginary part of the optical constant k and optical reflectivity change (ΔR) after laser irradiation are shown in Fig. 2. Both optical properties, which are known to correspond to the degree of damage of the substrate,^{7,8} decreased monotonically with the increase in irradiation time. The laser irradiation time, necessary for the damaged layer to attain the crystalline state, decreased as the substrate dopant concentration increased. These features were in close agreement with the electrical activation process of implanted ions.

The dependence of annealing behavior of an implanted layer on the dopant concentration of the substrate can be explained by considering the absorption mechanism of CO₂ laser light in silicon. The CO₂ laser wavelength, i.e., 10.6 μm, is, of course, longer than the absorption edge (1.1 μm) of crystalline silicon. Light absorption in this region occurs through the free-carrier absorption mechanism¹⁰ so that the absorption of CO₂ laser light increases with the increase in the substrate doping density. Consequently, annealing efficiency during CO₂ laser irradiation is to be enhanced by the increase in substrate doping density.

In order to confirm the present assumption, CO₂ laser light was irradiated simultaneously with uv light excitation on specimen having a background doping density of $1.4 \times 10^{14} \text{ cm}^{-3}$. Surface carrier concentrations and the de-

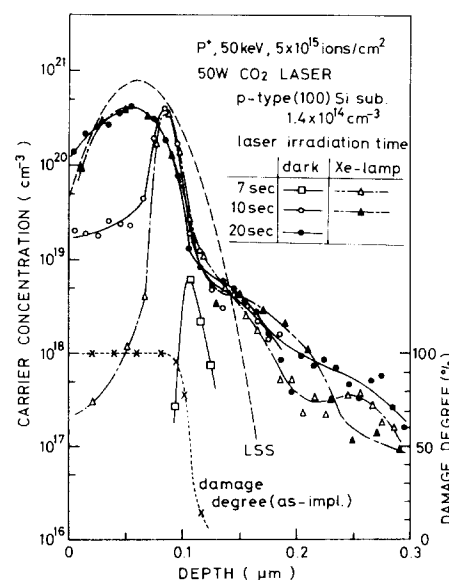


FIG. 3. Carrier concentration profiles after laser irradiation in the dark (\square, \circ, \bullet) under uv light excitation ($\triangle, \blacktriangle$) measured for specimen with a $1.4 \times 10^{14} \text{ cm}^{-3}$ substrate doping density. Phosphorus concentration profiles calculated by LSS theory and degree of damage before annealing (\times) are also shown.

degree of damage after irradiation are indicated in Figs. 1 and 2, respectively, as broken lines.

The irradiation time required to obtain full electrical activation or the recovery of a damaged layer to the crystalline state decreased under uv light excitation. Since uv light excitation is known to increase free-carrier concentration through a band-to-band transition mechanism, these experimental results are considered to confirm the present assumptions regarding the annealing mechanism.

Carrier concentration profiles after laser irradiation in the dark or uv light excitation were measured for a specimen having a dopant concentration of $1.4 \times 10^{14} \text{ cm}^{-3}$. They are shown in Fig. 3 for 7-, 10-, and 20-sec irradiation, respectively. Phosphorus concentration profiles (calculated by LSS theory¹¹) and the degree of damage before annealing (\times) are also shown in Fig. 3.

An amorphous layer (100% degree of damage) was formed continuously from the sample surface to a 1000-Å depth. During laser irradiation, the carriers were first generated in the deep regions where little damage was present. With the increase in the laser irradiation time, the region where the carriers were generated progressed from the amorphous-crystalline interface to the surface side of the implanted layer. These features agree with the electrical activation process observed in the furnace-annealed samples.¹² This fact indicated that carrier generation during CO₂ laser irradiation was caused by the solid-phase epitaxial regrowth of the amorphous layer.

In conclusion, we have shown that ion-implanted silicon layers may be annealed by infrared laser irradiation. In the process, CO₂ laser light was first absorbed by free carriers in the substrate silicon and turned into heat. Then, implanted ions were activated electrically through the solid-phase epitaxial mechanism.

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Efficiency enhancement in manganese-doped zinc silicate phosphor with AlPO₄ substitution

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Large increases in the efficiency of the conventional P1 phosphor (Zn₂SiO₄:Mn) have been achieved by substituting various combinations of III and V oxides for SiO₂, e.g., Zn_{2-*y*}Mn_{*y*}Si_{1-*2x*}Al_{*x*}P_{*x*}O₄. The photoluminescence efficiency of these phosphors exhibit strong dependence on the AlPO₄ substitution concentration *x* having highest efficiency for *x* = 0.5–1.5%. Cathodoluminescence and decay measurements show that such materials can have CL efficiency greater than the commercial zinc silicates and still have comparable persistence characteristics.

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Among known phosphors,¹ the manganese-activated zinc silicate is an efficient green emitting cathodoluminescent phosphor. This phosphor has been known for many years in mineral form as willemite² and in commercial products as P1.³ When P1 is codoped with As, known as P39, extremely long persistence is achieved.³ Because of their efficiency, electron burn resistance, and long-persistence characteristics, both P1 and P39 have been extensively used in many information-display cathode ray tubes and storage

tubes. In spite of their long history and extensive usage, little systematic work has been done to optimize or understand the luminescence process.

We have studied the effect of replacing part of the SiO₂ in Zn₂SiO₄ with various combinations of III and V oxides, which are model structures of SiO₂. In this paper we will report on substitutions of AlPO₄.

The luminescence efficiency is shown to be a strong function of the AlPO₄ substitution having highest efficiency