LASER TECHNIQUES IN PHOTOVOLTAIC RESEARCH*

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SUMMARY

High-power laser pulses are being used to replace the conventional high temperature furnace processing for the p-n junction formation step in high-speed, low-cost solar cell fabrication. Three different approaches to junction formation have been used: (1) laser annealing of ion-implanted Si in which laser radiation is used to remove the radiation damage and to recover the electrical activity in the implanted layer; (2) a process in which a thin film of dopant is first deposited on the substrate and then incorporated into the near-surface region by laser-induced diffusion; and (3) a process in which a heavily doped amorphous silicon layer is deposited on the Si substrate and epitaxially regrown from the melted substrate layer by laser radiation. We have demonstrated that all three methods provide suitable candidates for high efficiency Si solar cells.

INTRODUCTION

Approximately two years ago at the photovoltaic conference in Luxembourg, we described the use of high-power laser pulses to anneal the lattice damage in ion-implanted Si solar cells (ref. 1). We demonstrated that pulsed laser annealing is superior to conventional thermal annealing for the removal of lattice damage, for the recovery of electrical activity, and for the preservation of the minority carrier lifetime in the substrate, and we showed that this superiority resulted in improved solar cell performance. Pulsed laser annealing is now understood (ref. 2) to take place by a mechanism involving the ultrarapid melting of the entire damaged layer and subsequent liquid-phase epitaxial regrowth from the underlying perfect substrate. The dopant profiles are usually broadened considerably by pulsed laser annealing and this can be readily explained quantitatively by dopant diffusion in the molten state. An understanding of the importance of near-surface melting by laser heating led to the development (refs. 3-6) of two other laser-assisted junction formation techniques, i.e., laser-induced diffusion of dopant films and laser-induced recrystallization of doped amorphous films to form epitaxial junctions. These techniques are important because they are much simpler and more easily automated processes than either thermal diffusion or ion implantation. This is

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particularly advantageous for solar cells which require high-volume, low-cost fabrication processes to become economically competitive in terrestial applications. In this paper we review and compare the three laser-assisted junction formation techniques and discuss their applications to solar cell fabrication. Throughout this work, the laser annealing was performed in air with the Q-switched output of a ruby laser (λ = 0.694 μ, τ = 15-60 nsec). After the samples were exposed to the laser pulses, the perfection of the emitter regions was studied by transmission electron microscopy (TEM), and their electrical parameters were determined by van der Pauw measurements. The dopant profiles were obtained by secondary ion mass spectrometry (SIMS) or anodic oxidation and stripping technique. The resulting junction characteristics were studied by I-V and C-V measurements on mesa diode structures. Finally solar cells were fabricated and tested under AM1 illumination.

JUNCTION FORMATION BY ION IMPLANTATION AND LASER ANNEALING

In this method, energetic dopant ions are allowed to impinge on a Si substrate and laser radiation is used to remove the radiation damage and to bring the dopant ions into electrically active substitutional sites. The resulting dopant profile and junction depth are determined by the as-implanted profile, which is controlled by the stopping power for the dopant particles in silicon and the implantation energy, and by the duration of the laser-induced surface melting which is controlled by the laser parameters such as energy density and pulse duration time. The influence of the laser energy density on the dopant profile behavior is given in figure 1 which shows results for samples implanted with ^{11}B (35 keV, 1 x 10^{16} cm^{-2}) and subsequently annealed with laser pulses in the energy density range of 0.64 J/cm^2 to 3.1 J/cm^2. At a laser energy density $\sim$.6 J/cm^2, the boron profile is indistinguishable from that of the as-implanted specimen. Evidence that the annealing was incomplete in this sample was obtained from van der Pauw measurements and from TEM which showed that only $\sim$ 30% of the expected electrical activity had been obtained, and that significant damage in the form of dislocation loops remained. Complete annealing was achieved with energy densities of 1.1 J/cm^2 and greater; the profiles were then almost flat topped in the surface region with the penetration depth increasing as the energy density was increased. Figure 2 gives the comparison of dopant profiles obtained from samples implanted with boron at 5 keV and 35 keV and annealed with laser pulses of 1.7 J/cm^2. These results indicate that in order to obtain a defect-free shallow junction by the ion-implantation, laser-annealing technique, the implantation energy should be kept low and the laser energy just high enough to melt the surface layer which contains the damaged region. Solar cells with conversion efficiencies of 14-15% can be routinely fabricated by this technique. Parameters of a typical cell made from Si implanted with ^{75}As$^+$ (5 keV, 2 x 10^{15} cm^{-2}) and annealed with one pulse of a ruby laser are I_{sc} = 33.6 ma/cm^2, V_{oc} = 565 mV and FF = 0.76 and a resulting conversion efficiency of 14.5%. The cells were fabricated with single-layer Ta_2O_5 antireflection coatings and no back surface fields.

JUNCTION FORMATION BY LASER-INDUCED DIFFUSION

In this technique, thin (50-100 Å) films of dopants such as boron and aluminum are first vacuum-deposited on the substrate and then driven into the near-surface region by laser-induced surface melting and diffusion. Transmission electron microscopy and electrical measurements show that the dopants are dissolved in the silicon lattice and electrically activated. Resultant emitter regions with appropriate sheet resistivities (30-100 Ω/□) for solar cell applications can be obtained and the dopant profiles are nearly ideal for high efficiency cells. Figure 3 gives the boron concentration profile after laser irradiation with pulses of 1.5 J/cm^2. This profile has a high dopant concentration near the surface region and an intermediate region decreasing toward the junction. The high potential barrier near the surface will reflect the minority carriers from the surface and minimize surface recombination losses. The results of I-V and reversed-biased C-V measurements on Al-deposited, laser-annealed mesa diodes are given in figure 4. The near unit value of A, the small reverse-bias current and the good agreement between the measured and expected junction potentials suggest that a defect-free junction was obtained. Solar cells were fabricated and tested and the efficiencies were found to be comparable to or slightly lower than those of the ion-implanted laser-annealed cells. The effects on cell performance of impurities in the dopant source and of surface contamination during deposition are not clear at the present time.

FORMATION OF EPITAXIAL p-n JUNCTION BY PULSED-LASER RADIATION

In a more recent study, we have demonstrated that laser radiation can be used for epitaxial regrowth of a doped amorphous silicon layer deposited on a silicon substrate. A single pulse from a ruby laser with an energy density of 1.8 J/cm^2 was sufficient to recrystallize, with almost perfect crystallinity, an As-doped amorphous silicon layer deposited on a (100) substrate to a depth of about 3000 Å. Junction characteristics determined by I-V and C-V measurements showed that a perfect junction with a low leakage current was achieved. Use of this technique for junction formation provides many advantages normally attributed to ion implantation, such as relatively easy control of dopant concentration and junction depth. Figure 5 shows dopant profiles measured by Hall effect measurements in combination with anodic oxidation and stripping techniques for the cases of 1000 Å and 2000 Å deposited layers annealed with pulses of 1.55 J/cm^2 and 1.78 J/cm^2, respectively. The dopants have spread deeper into the substrate in a manner very similar to dopant redistribution in As-implanted laser-annealed samples (ref. 2). The solid line in the figures are calculated profiles using techniques described in reference 2. The liquid phase diffusion of As was calculated from ideal as-deposited profiles (dotted lines) without considering the possible complications due to thin interfacial oxygen layers between the substrate and deposited layers. The agreement between the experimental and calculated profiles is very good. From these results, it appears that junction parameters can easily be controlled with this method by a variation of the dopant concentration in the evaporant source, the thickness of the deposited layer, and the energy density of the laser radiation. Solar cells have not yet been fabricated with this technique. However, from the results described above, we anticipate that it should provide another alternative method for high efficiency solar cell fabrication. Extensive studies of the effects of substrate orientation on recrystallization, interfacial problems such as the presence of SiO_2 or hydrocarbons, and the influence of the various dopant impurities and residual gas atoms (such as H_2, N_2, and O_2) on the regrowth behavior are currently underway.

CONCLUSIONS

In conclusion, high-quality p-n junctions can be formed by the use of laser pulses to anneal radiation damage, induce diffusion, alloying, and regrowth of films deposited on silicon substrates. Due to the simplicity and low cost of this type of processing, we expect that the methods discussed here, after further development, will be extremely useful in the large-volume fabrication of high-efficiency solar cells.

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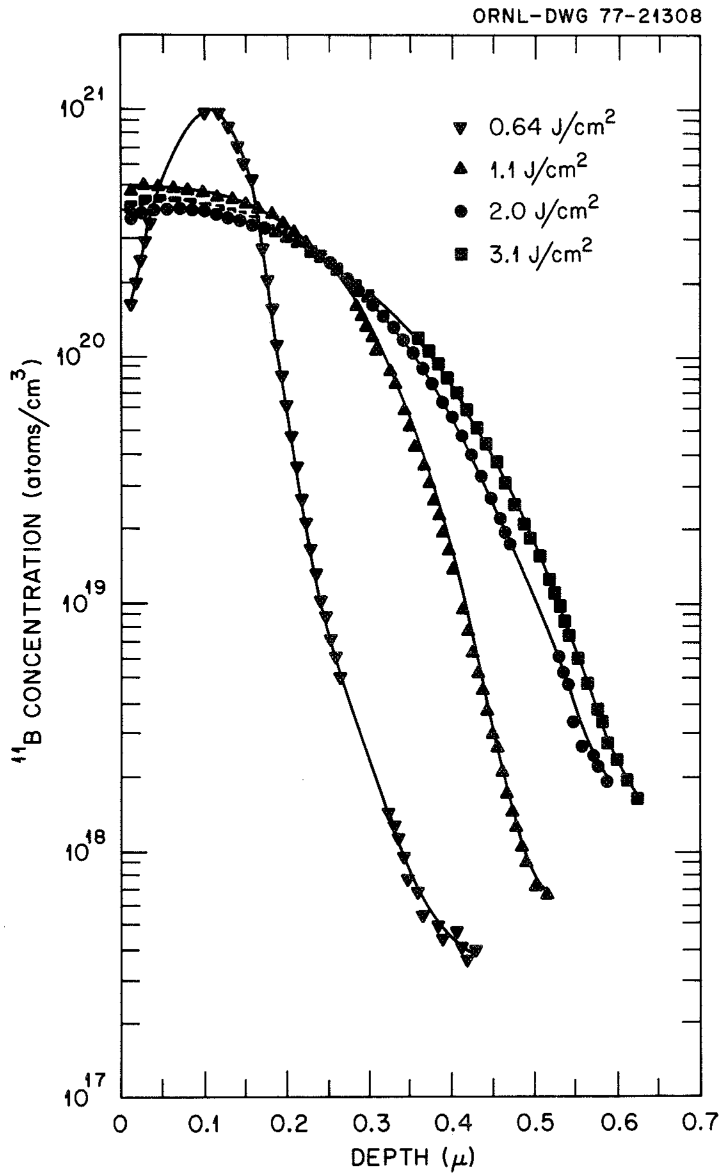

Figure 1. Comparison of ^{11}B (35 keV, 1 x 10^{16}/cm^2) profiles annealed by different laser energy densities.

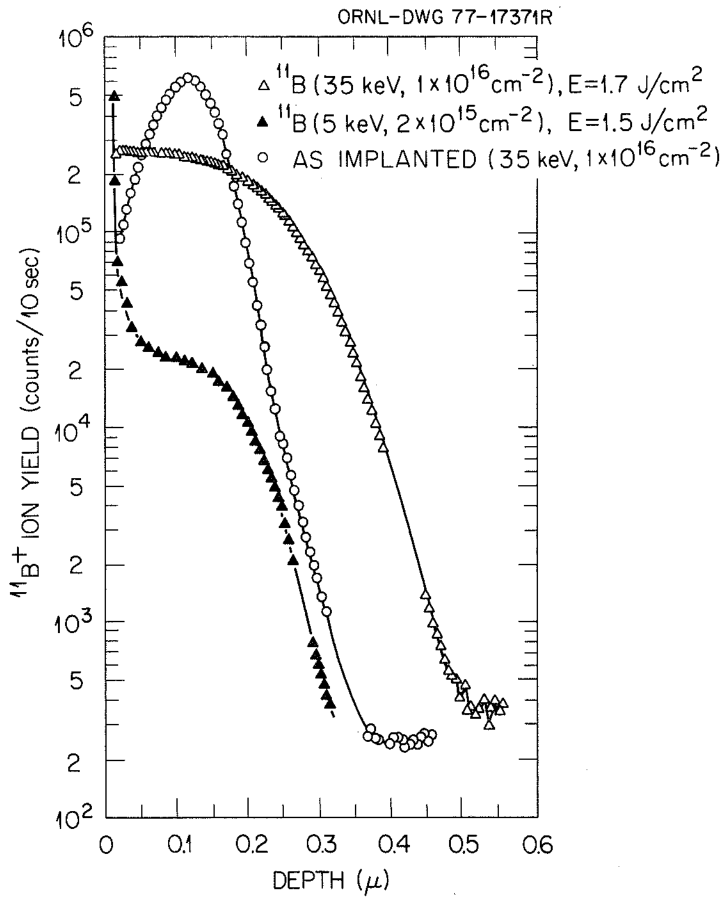

Figure 2. Comparison of ^{11}B (35 keV) and ^{11}B (5 keV) profiles annealed by laser energy density of 1.7 J/cm^2.

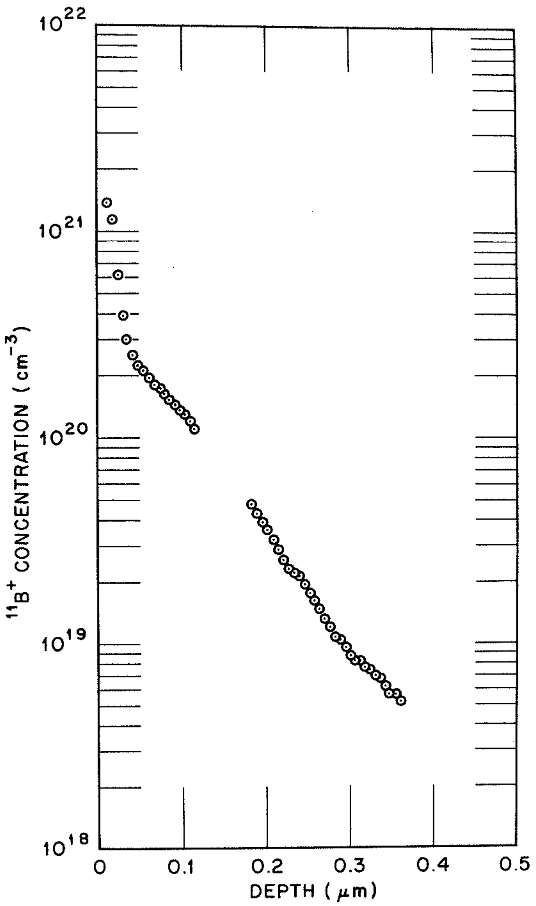

Figure 3. Depth profiles for boron-deposited, laser-annealed Si.

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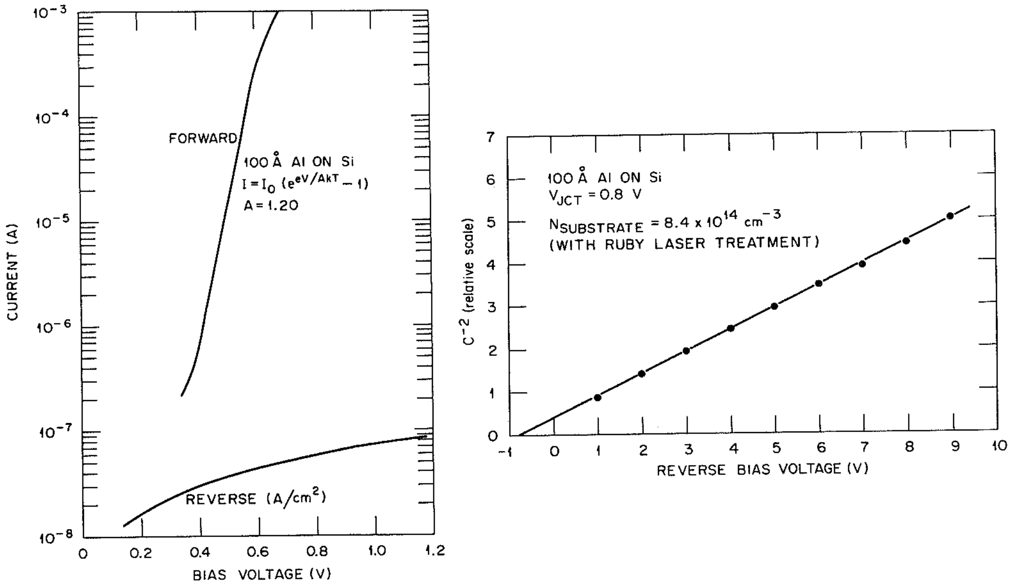

Figure 4. Dark I-V and reverse-biased C-V measurement on Al-deposited laser-annealed Si mesa diodes.

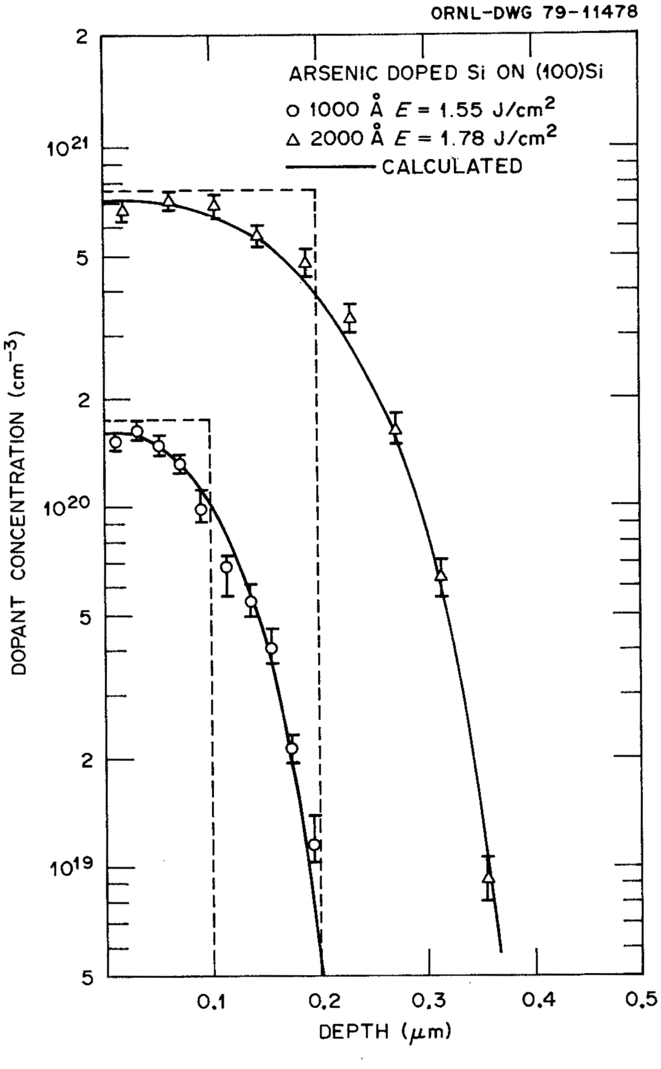

Figure 5. Comparison of experimental and calculated dopant profiles on 1000 Å and 2000 Å deposited layers after laser irradiation.