Semiconductor processing with excimer lasers

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SEMICONDUCTOR PROCESSING WITH EXCIMER LASERS[*]

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ABSTRACT

The advantages of pulsed excimer lasers for semiconductor pro-
cessing are reviewed. Extensive comparisions of the quality of
annealing of ion-implanted Si obtained with XeCl and ruby lasers
have been made. The results indicate that irrespective of the large
differences in the optical properties of Si at UV and visible wave-
lengths, the efficiency of usage of the incident energy for anneal-
ing is comparable for the two lasers. However, because of the
excellent optical beam quality, the XeCl laser can provide superior
control of the surface melting and the resulting junction depth.
Furthermore, the concentrations of electrically active point defects
in the XeCl laser annealed region are 2-3 orders of magnitude lower
than that obtained from ruby or Nd:YAG lasers. All these results
seem to suggest that XeCl lasers should be suitable for fabricating
not only solar cells but also the more advanced device structures
required for VLSI or VHSIC applications.

INTRODUCTION

In the past few years, extensive research has been carried out
on the use of laser radiation to process semiconductor materials.[1]
The interest underlying this research is largely motivated by the
realization that laser processing may have significant advantages
over more conventional processing steps for the fabrication of many

semiconductor devices. Both pulsed and cw lasers have been used for
laser processing. However, because of the difference in annealing
mechanisms, i.e., liquid vs solid phase epitaxy, many properties
such as dopant diffusion and segregation, the extent of grain growth
in amorphous and polycrystalline material, and the concentrations of
residual defects in the laser recrystallized region are quite dif-
ferent for pulsed and cw laser annealed samples. In this paper, we
will concentrate our attention on the use of pulsed lasers for the
annealing of ion-implanted silicon. More specifically, we will make
extensive comparisons of the quality of annealing obtained with solid
state lasers (ruby, YAG, etc.) and the recently developed rare gas
halide excimer lasers (XeCl, XeF, etc.).

It is widely recognized that one of the major obstacles to the
development of pulsed-laser processing for practical applications in
the past has been the lack of suitable lasers. The pulsed lasers
most commonly used for semiconductor processing have been ruby (0.694
μm), frequency-doubled Nd:YAG (0.532 μm) or glass (0.531 μm), and
(more recently) alexandrite (0.700-0.818 μm) lasers. These solid-
state lasers have certain limitations for high-throughput processing
of large area devices. Foremost among these limitations is the spa-
tial inhomogeneity of the energy density in the pulses. Inhomogene-
ities may be produced by a number of effects, e.g., multimode opera-
tion in which only a few modes are present, residual strains in the
large solid-state laser rods, and thermal lensing. In addition, the
coherent nature of the laser radiation may cause diffraction pat-
terns to be produced by optical components, dust particles, and
other sources of scattered radiation. Diffraction-related structure
is frequently observed on surfaces irradiated with solid-state
lasers. In order to reduce the pulse inhomogeneities to acceptable
levels, it is necessary to transmit the beam through a beam homoge-
nizer. Homogenization has been carried out using a variety of opti-
cal devices, including ground glass diffuser plates, bent quartz
light pipes, and segmented cylindrical lens. These techniques pro-
duce either high transmission losses or interference fringes from
the overlapping beams. Furthermore, the devices can only partially
reduce the inhomogeneities, and they add to the complexity of the
processing. Other drawbacks of solid-state lasers include low pulse
repetition rates for systems with large diameter rods (because of
the heat dissipation problem in the insulating crystals) and low
overall energy conversion efficiency. These difficulties appear to
put unacceptable limitations on device throughput rate and cost for
many applications.

Gas lasers have few of the drawbacks of solid-state lasers, and
it is now clear that the XeCl excimer laser used in our research has
many of the characteristics needed for the efficient laser processing
of semiconductors. Because of the large discharge volume and the
short wavelengths involved, the optical cavity of a UV excimer laser
can support oscillations of the electromagnetic field composed of a
very large number of modes. A uniform beam with reduced spatial
coherence is obtained and, as a result, interference effects caused
by the coherent nature of normal laser radiation are nearly elimi-
nated. This special characteristic of excimer lasers has been

recently demonstrated to be advantageous for UV lithography,[2] and this same characteristic is highly desirable in the laser processing of semiconductor devices. Recent developments in excimer laser technology[3] suggest that lasers with reasonably high energy per pulse and pulse repetition rates in the kilohertz range, or with single pulse output approaching 10^3 J, can be designed and constructed. The potential importance of these developments for the laser processing of materials is obvious, provided good spatial uniformity and pulse-to-pulse reproducibility can be maintained.

A careful and detailed evaluation of the suitability of excimer lasers for processing semiconductors, especially Si, is necessary because of the large differences in the optical properties of silicon at UV and visible wavelengths.[4] For example, the optical absorption coefficient α of silicon at the 308 nm wavelength of the XeCl laser is $\sim 10^6$ cm^{-1} and the reflectivity R is $\sim 60\%$; neither quantity depends strongly on temperature. In contrast, the absorption coefficients for ruby and frequency-doubled YAG lasers are highly temperature dependent within the range 10^3-10^5 cm^{-1}, while R = 35-45% and is also somewhat temperature dependent. In spite of these large differences, we have found the quality of the annealing, in terms of removal of lattice damage, electrical activation of dopants, dopant profile behavior, and p-n junction characteristics, to be very similar for the two types of lasers.[5] However, the extremely good spatial uniformity of the excimer laser beam, the reduced coherence of the radiation, and the wide energy window between the annealing and damage thresholds that results from these two characteristics, give excimer lasers clear advantages over solid state lasers for many types of semiconductor processing. In fact, our results of recent studies using DLTS (deep level transient spectroscopy) on Schottky diodes show that the density of deep level defects in the excimer laser annealed samples can be as low as $\sim 5 \times 10^{11}$ cm^{-3} which is about 2-3 orders of magnitude lower than the reported defect density in samples annealed by pulsed solid state lasers.[6] In our work, Si solar cells have been processed both by ruby and excimer lasers; the results indicate that XeCl laser processed cells generally give superior performance.

II. REVIEW OF PULSED LASER ANNEALING

Before we present our experimental results, a brief review of the fundamentals of pulsed laser annealing and its potential applications will be given in this section. Even though solid state lasers (ruby or Nd:YAG) were used exclusively in this earlier work, the results to be demonstrated in the next section indicate that the annealing characteristics obtained with UV excimer lasers and solid state lasers are virtually the same. Therefore, all the features of pulsed laser annealing described here should be readily applicable to annealing with a XeCl laser.

Many research efforts to date in this area of solid state physics have been directed toward obtaining a fundamental understanding of pulsed laser induced ultrarapid surface melting and solidification. Both theoretical[7] and experimental[8] results indicate that in

silicon the melt durations are typically in the range of a few tens
to a few hundreds of nanoseconds and the solidification rates are of
the order of meters per second. In such melting and resolidifica-
tion regimes, substantial dopant diffusion in the melt can occur and
recrystallization takes place under conditions that are far from
thermodynamic equilibrium. Many phenomena such as nonequilibrium
segregation, formation of supersaturated substitutional alloys, etc.
have been observed and studied.[7] In spite of the nonequilibrium
nature of the annealing process, high quality, dislocation-free,
electrically active layers are readily produced. However, several
reports[6] have indicated that high densities of electrically active
point defects smaller than the detection limit of TEM (transmission
electron microscopy) are present in the annealed region. The origin
of such defects was at first thought to be related to the ultrarapid
quenching. However, such an hypothesis cannot be entirely correct
because such high defect densities are not observed in excimer laser
annealed samples. These results will be discussed later in this
paper. Other than the use of pulsed lasers to remove ion implanta-
tion damage, potential applications include the use of laser radia-
tion to induce dopant diffusion from solid,[9] liquid[10] and gaseous[11]
sources, to dissolve second phase precipitates,[12] to produce super-
saturated alloys,[13] to form metal silicides,[14] to promote grain
growth,[15] to reduce sheet resistivity in polycrystalline Si,[16] to
improve interface properties in SOS devices,[17] and to realize back-
surface damage gettering.[18] Irrespective of so many potential
applications, the device that has been fabricated most successfully
so far by pulsed-laser annealing is the Si solar cell,[19] which can
tolerate relatively large variations in the annealing energy density
and does not have a complex surface structure. For the more complex
structures, such as those used in the MOS devices of VLSI and VHSIC
(very high speed integrated circuit) technologies, laser annealing
is still in its infancy. The recent trend in integrated circuit
development has been toward low-temperature processing, with the
goals of obtaining shallower junction depth, higher operating speed,
and increased packing density; it is believed by many device physi-
cists that laser annealing may hold the key to the attainment of
these goals. Processing areas associated with VLSI for which laser
annealing has shown some encouraging results are 1) the reduction of
the overlap capacitance in source-drain regions of short-channel
MOSFET's as a result of the elimination of lateral diffusion
effects[20], 2) the reduction of sheet resistance in polycrystalline
Si to increase the conductivity of interconnects in poly-gate MOS
structures,[16] and 3) the improvement of MOS recovery lifetime by
laser back surface damage gettering.[18] These results, though
encouraging, must still be considered preliminary because solid
state lasers, with their inherent limitations, were used in the
studies. Some of the questions which arise about the fabrication of
complex devices with solid state lasers are 1) can the laser beam be
controlled well enough to provide a particular junction depth to high
accuracy (say ± 4%)? 2) Can the devices tolerate the electrically
active defects introduced and/or remaining in the laser annealed
region? 3) Can the problems associated with the simultaneous laser

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irradiation of different device areas composed of polysilicon, SiO_2, and ion-implanted amorphous Si be solved? 4) Can the processing give high enough throughput rates? It seems that, with the superior characteristics of excimer lasers, some of these problems encountered with solid state lasers may be easily resolved.

III. EXPERIMENT

An x-ray preionized, discharge-pumped XeCl laser designed and constructed by Helionetics, Inc. was used in the work reported here. The laser was designed so that the pulse duration time τ_ℓ can be varied between 20-90 nsec (FWHM,~trapezoidal pulse) simply by changing the ratio of gas mixtures. The total area of the laser beam is 3 cm x 2.5 cm. The energy output is ~2.5 J at 75 nsec, and the beam was focused to give the desired energy density. The pulse repetition rate of the present system is 1 Hz, but an advanced laser system with 100 Hz repetition rate and pulse energy > 1 J is currently under construction. With this system, an annealing throughput of ~50 cm^2 sec^{-1} should be possible. For comparison studies, a commercially available Apollo Q-switched ruby laser which gives an energy output of ~12 J (multimode) and τ_ℓ of 25 nsec (FWHM, gaussian pulse) has been used in our work. Polished (100) Si samples implanted with As, B or Si at various energies to a dose up to $1x10^{16}$ cm^{-2} were used in this study. All annealing was performed in air. No beam homogenizer was used during XeCl laser annealing, but a ground glass diffuser plate was used while annealing with the ruby laser. The depth of melting and crystal perfection of the laser regrown layers were determined by TEM. The dopant redistribution after laser annealing was examined by secondary ion mass spectroscopy (SIMS). The electrical properties of the laser-regrown layer were obtained from van der Pauw measurements and dark I-V characteristics. The electrically active defects were studied by DLTS. Laser-processed Si solar cells were fabricated by using a low-cost, gaseous-discharge implantation technique, followed by either ruby or excimer laser annealing, to form the front junction. The back surfaces were made degenerate by vacuum deposition of ~70 A of antimony followed by laser annealing. Ta_2O_5 and MgF_2 were used for double-layer antireflection coatings.

IV. COMPARISON OF ANNEALING CHARACTERISTICS OF XeCl AND RUBY LASERS

Surface Morphology
An important concern in the use of pulsed lasers in semiconductor processing is the surface morphology after laser treatment. The preservation of a flat, featureless surface is extremely important in devices if multi-step processing is required. Apart from hot spots and diffraction-induced localized surface damage, a periodic surface structure has been observed[21] frequently in ruby or Nd:YAG laser annealed samples. This periodic pattern is thought to be due to heating by a standing wave resulting from the interference of the incident and the scattered wave.[22] Figures 1a and 1b show typical surface structures observed after ruby laser annealing. A beam
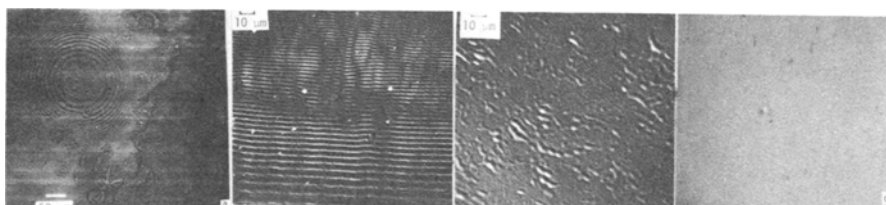
Fig. 1. Surface morphology of laser annealed Si surface.
a) EBIC image showing diffraction pattern and hot spots directly
    from multimode beam of a ruby laser (E_ℓ = 1.6 J/cm^2),
b) optical micrograph showing periodic ripple structures directly
    from multimode beam of a ruby laser (E_ℓ = 1.8 J/cm^2),
c) optical micrograph showing randomly distributed surface ripples
    from multimode beam of a ruby laser through a diffuser plate
    (E_ℓ = 1.8 J/cm^2),
d) optical micrograph showing the smooth surface directly from
    multimode beam of a XeCl laser (E_ℓ = 3.5 J/cm^2, τ_ℓ - 55 nsec).

homogenizer such as a ground glass diffuser plate can effectively
remove the major intensity variations. However, the diffuser plate
scatters most of the light into a relatively narrow cone about the
incident beam direction and can produce focussing effects on a fine
scale. This microfocussing can create randomly distributed surface
ripples, as shown in Fig. 1c. These surface ripples can be elimi-
nated only when the sample is placed farther from the diffuser with
reduced energy density ($\leq$1.6 J/cm^2). On the other hand, the surface
morphology of the samples after XeCl laser annealing at energy den-
sities up to $\sim$3-4 J/cm^2 (depending on the pulse duration time) is
smooth and flat (Fig. 1d). No unusual surface features caused by
hot spots, diffraction patterns or other interference effects are
observed. To evaluate the uniformity of the laser beam on a micro-
scopic scale, the damage interfaces in annealed and unannealed
samples of B (200 kV) implanted Si were examined by TEM. Figure 2
shows cross section micrographs of samples annealed with the ruby
laser through a diffuser plate and with the XeCl laser at 2.5 J/cm^2.
It is clearly seen that XeCl lasers provide a much more uniform
interfacial layer. In contrast, a variation in melt depth as large
as $\sim$25% in 2 μm region is observed in ruby laser annealed sample.

Dopant Profiles
     A comparison of laser-induced surface melting and dopant dif-
fusion in ruby and XeCl laser-annealed samples of $^{11}B^+$ (35 kV,
1×10^{16} cm^{-2}) implanted Si was made by SIMS profiling. Both lasers
had the pulse duration time of $\sim$25 nsec, although the pulse shapes
were quite different. Figure 3 shows the dopant redistribution in
samples annealed with the two lasers at energy densities of 1.5
J/cm^2 and 2.0 J/cm^2. It is interesting to see that at the same
energy density, the resulting dopant profiles arising from the two
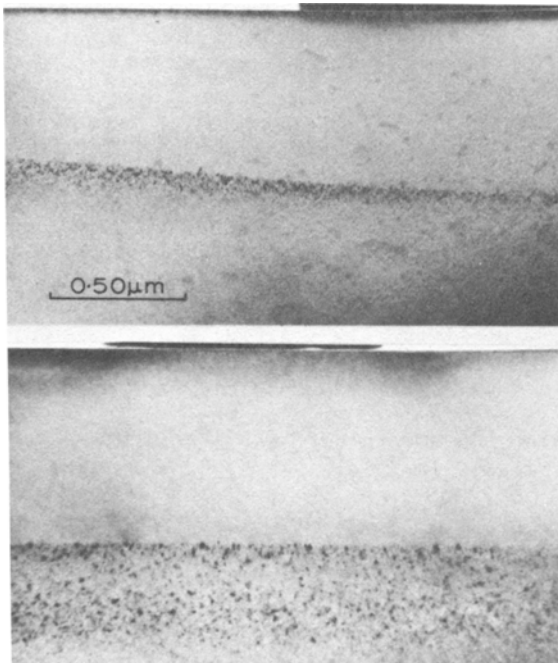lasers are almost identical. These results strongly suggest that

Fig. 2. TEM micro-
graphs showing the
annealed and unan-
nealed damage inter-
faces in B (200 kV)
implanted Si.

a) Ruby laser
   annealing at
   2.5 J/cm^2,

b) XeCl laser
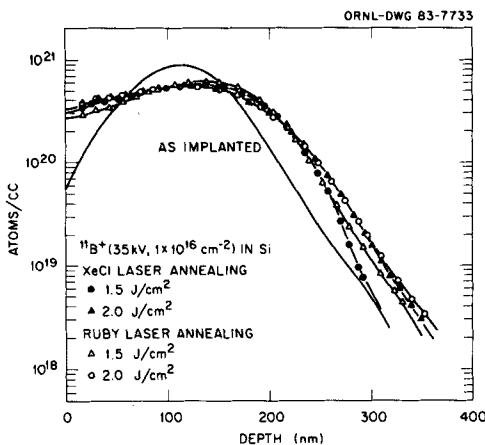   annealing at
   2.5 J/cm^2.

Fig. 3. Comparison of boron
implanted dopant profiles
annealed at two different
laser energy densities with
the ruby and XeCl lasers.

regardless of the large differences in the optical properties of Si
at UV and visible wavelengths, the efficiency of usage of the inci-
dent energy for melting Si surface regions to comparable depths is
approximately the same for the two lasers with similar pulse dura-
tion times. The quality of the annealing of these samples was sub-
sequently examined by TEM and by van der Pauw measurements. In all
cases, a dislocation-free, fully electrically activated laser-
regrown layer was observed. Because of the wide energy window in
excimer laser annealing, deep junction profiles can be readily

obtained with multiple pulses of laser radiation. This result is illustrated in Fig. 4. It shows that a sample with junction depth close to 0.9 μm can be achieved with 10 laser pulses at 3.5 J/cm^2 without any noticeable surface damage. Comparable junction depths could be obtained with ruby laser pulses, but the prevention of surface damage would be extremely difficult if not impossible.
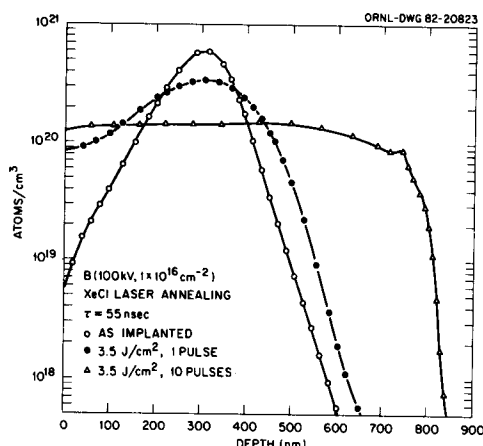

Fig. 4. SIMS profiles for boron in silicon after XeCl laser annealing at 3.5 J/cm^2 with 1 and 10 pulses.

Electrically Active Defects

The laser-annealed regions in our samples are dislocation-free under TEM observation and have good electrical properties (sheet resistivity and mobility) under van der Pauw examination, but as already mentioned, it has been reported[6] that high concentrations (10^{13}-10^{15} cm^{-3}) of electrically active defects were detected by DLTS in samples irradiated with pulsed ruby and Nd:YAG lasers. The existence of these defects may have a large influence on device performance. In the study of XeCl laser annealed samples, we found that electrically active defects are present at concentrations much lower than those reported for samples annealed with solid state lasers. Figure 5 shows a typical DLTS spectrum from Schottky diodes made on Si (10 kV, 5x10^{15} cm^{-2}) implanted, B-doped silicon samples after XeCl laser (25 nsec) annealing at 2 J/cm^2. A single defect level located at 0.38 eV above the energy of the valence band E_v is observed. The concentration of this defect is $\sim$5x10^{11} cm^{-3}. These results strongly suggest that the existence of electrically active defects in laser regrown regions is not related solely to the regrowth velocity V, since melting model calculations[23] show that the value of V from the two lasers with the same pulse duration times are very similar. The mechanism of defect formation in samples annealed with solid state lasers apparently needs considerable further study.
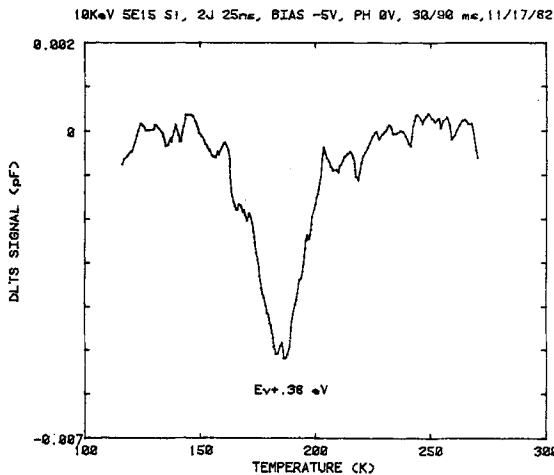
10K.V 5E15 Si, 2J 25n≤, BIAS -5V, PH 0V, 30/90 m≤,11/17/82

Fig. 5. DLTS spectrum of Si (10 kV, 5x10^{15} cm^{-2}) implanted p-type Si after XeCl laser annealing at 2.0 J/cm^{2}.

V. EFFECT OF PULSE DURATION ON THE ANNEALING

Advances in excimer laser technology indicate that, in addition to the capability for scaling, a laser system can be designed so that the pulse duration time τ_ℓ can be adjusted over a range from ten to several hundred nsec. Variation of τ_ℓ over this range with solid state lasers is difficult, if not impossible. Melting model calculations[7,23] show that, for the same energy density E_ℓ, the depth of melting increases with decreasing pulse duration, especially for E_ℓ near the threshold for surface melting. The influence of the regrowth velocity on the quality of laser regrown layers and the optimum τ_ℓ for energy-efficient semiconductor processing have not yet been investigated in detail.

In this section, we discuss the effect of τ_ℓ on the annealing of ion-implanted Si by comparing the melting depth, crystal perfection, dopant profiles, and electrical properties of samples annealed with a XeCl laser with E_ℓ in the range of 0.5-3.0 J/cm^{2} and for τ_ℓ of 25 and 70 nsec. As anticipated from the model calculations,[23] the results indicated that 25 nsec pulses are more energy efficient in annealing of ion-implanted damge than are 70 nsec pulses. The melting depth as a function of laser energy density for the two laser pulses as determined from TEM is plotted in Fig. 6. It can be seen from the plot that at the same energy density, considerably deeper melting is achieved with 25 nsec pulses than with 70 nsec pulses, which is in good qualitative agreement with calculations. Figure 7 shows the effect of pulse duration time on the dopant profile redistribution of 100 kV B-implanted Si annealed with E_ℓ = 2.5 and 3.0 J/cm^{2}; these results demonstrate that shorter laser pulses provide deeper dopant spreading, as expected. However, it is interesting to see that a very abrupt dopant profile was obtained on the sample that was annealed with 70 nsec pulses at an energy density just above the threshold for complete annealing (i.e., 2.5 J/cm^{2} in this case). Similar results[5] were also observed in arsenic implanted
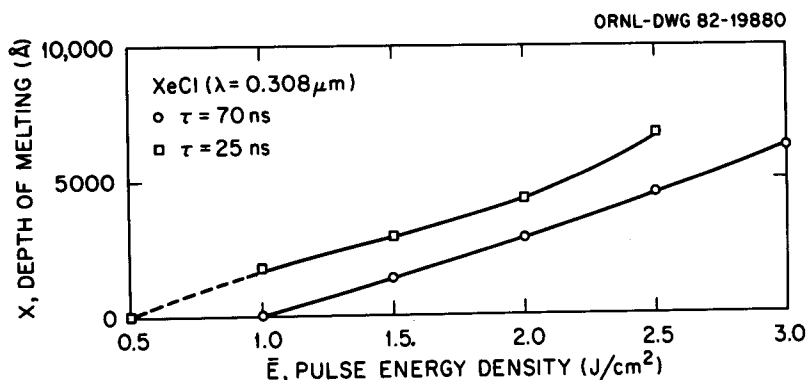
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Fig. 6. The melting depth as a function of laser energy density for 25 and 70 nsec laser pulses as determined from TEM.
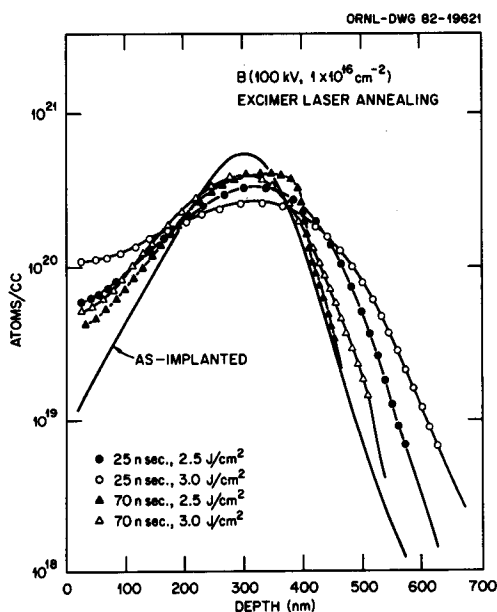

Fig. 7. A comparison of concentration profiles of B in Si after XeCl laser annealing at 2.5 and 3.0 J/cm² with 25 and 70 nsec pulses.

samples. This phenomenon has not been seen in ruby or short pulse (25 nsec) XeCl laser annealed samples. The quality of annealing, in terms of crystalline perfection of the regrown layer (by TEM), junction characteristics (by dark I-V measurements), and residual defects (by DLTS), is very similar for the two pulse durations. From these results, we can conclude that for a device, in which a junction depth deeper than ∿1000 A is desired, a laser with shorter pulse duration is more energy efficient for annealing. However, longer pulse durations may have the advantage of providing shallow surface melting (200-500 A) and a more abrupt dopant profile, which

is especially critical for high switching speed devices that require very sharp doping changes on the scale of ~200 A. Research related to this possibility is currently underway.

VI. EXCIMER LASER PROCESSED Si SOLAR CELLS

Beam processing (ion or gaseous discharge implantation, laser or e-beam annealing) for solar cell production is thought by many to be highly promising because of the expected ease of automation and the likely realization of improved control of a number of critical parameters (e.g., junction depth, sheet resistivity, lifetime), which will result in increased yield and improved cell performance. Recently we have demonstrated that the combination of glow discharge implantation and XeCl excimer laser annealing for solar cell fabrication is especially suitable for terrestrial photovoltaic applications because of the potential for low cost and high throughput.[24] Polished 1-3 Ω-cm n-type FZ Si wafers were implanted either by BF_3 glow discharge implantation at an energy of 1 kV to a dose of 6×10^{15} cm^{-2} or with B by conventional ion implantation equipment at 5 kV to the same dose. Each wafer was then cut into six 1x2 cm samples. Half of the samples were annealed with the ruby laser and the other half with the excimer laser. The back surfaces were made degenerate by laser-induced diffusion of Sb. Evaporated Ti-Pd-Ag metallization was used to form the front and back contacts. Under optimum annealing conditions, all of the cells had open circuit voltages, V_{OC} (measured at 28°C) in the range 600-610 mV and fill factors in the range 0.77-0.80. However, there were noticeable differences in the short circuit currents, J_{SC}. In general, the excimer laser annealed cells showed better J_{SC} than did the ruby laser annealed ones; whereas among the excimer laser annealed samples, the BF_3 implanted cells had higher J_{SC} than did the B (5 kV) implanted cells. This difference can be understood from _internal_ quantum efficiency measurements on the cells before the application of AR
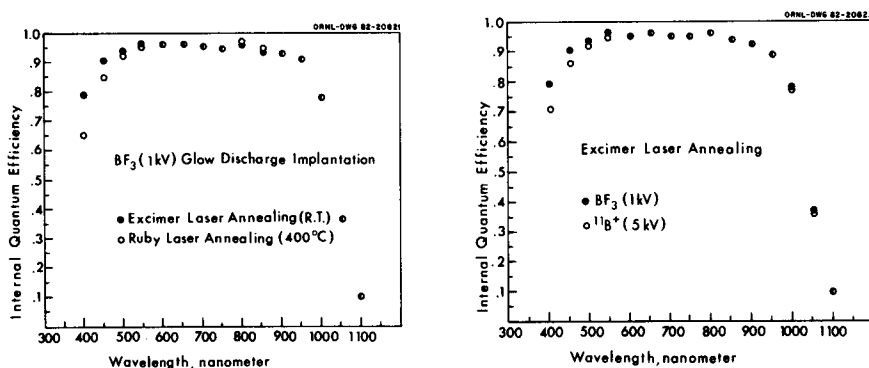

Fig. 8. Comparison of internal quantum efficiency between cells fabricated from a) excimer and ruby laser annealing, and b) BF_3 (1 kV) and $^{11}B^+$ (5 kV) implantation.

coatings. The results, shown in Fig. 8, clearly indicate that the BF_3-implanted, excimer laser-annealed cells have the highest blue response. This can be attributed to the high quality shallow junction formed from the shallow implantation (1 kV) and the extremely uniform annealing obtained with the excimer laser. The best discharge-implanted, excimer laser-annealed cell obtained so far has the parameters V_{OC} = 610 mV, J_{SC} = 34.7 mA/cm^2, FF = 0.79, which result in an efficiency of 16.7%. This efficiency is comparable to the highest efficiency Si solar cells made by the most sophisticated conventional methods.

VII. CONCLUSIONS

We have demonstrated that regardless of the large differences in the optical properties of Si at the wavelengths of the radiation from a XeCl laser and visible lasers such as ruby or frequency-doubled Nd:YAG, the efficiency of usage of the incident energy and the quality of annealing is very similar. However, because of the good optical quality of the beam and perhaps because of the trapezoidal (rather than gaussian) temporal shape of the excimer laser pulses, excellent annealing with superior control of surface melting and the resulting junction depth can be obtained without the use of beam homogenizers and substrate heating. This provides important simplifications for application of laser annealing to device processing. We have demonstrated that high efficiency Si solar cells can be readily fabricated by laser processing. Furthermore, we found that the concentrations of electrically active point defects, measured by DLTS, in the XeCl laser-annealed regions are 2-3 orders of magnitude lower than those in regions annealed with solid state lasers. These features of XeCl lasers seem to suggest that this type of laser should be suitable for processing not only solar cells but also the more advanced device structures needed in VLSI and VHSIC applications.

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