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Crowder[2] have proposed to estimate $F_A$ from

$$F_A = \bar{E} n_2 \left(\frac{dE}{dx}\right)_0^{-1}, \quad (1)$$

where $\bar{E}$ is the effective energy to displace a target atom, $n_2$ is the number of target atoms per unit volume, and $(dE/dx)_0$ is an approximation for the nuclear energy loss per unit path length. Although Eq. (1) implies that all of the target atoms must be displaced and thus will result in too high a value, we may use it to compare the results for the three compounds. E was taken as twice the displacement energy given by Thompson and Walker.[12] With E = 19/19.5/20 eV for GaAs/$GaAs_{0.6}P_{0.4}$/GaP, we obtained $F_A = 11.5/10/9.5 \times 10^{13}$ ions/cm$^2$. These values differ from the experimental results by a factor of about 0.56, the ratios being approximately the same. The target temperature necessary to suppress the formation of an amorphous layer increases in the sequence GaP/$GaAs_{0.6}P_{0.4}$/GaAs.

In conclusion, we have shown that reliable data about radiation damage and annealing can be provided by electron-beam-absorption measurements. New data have been presented for GaP and $GaAs_{0.6}P_{0.4}$ which compare well with known data for GaAs and GaP.

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# Time-resolved reflectivity of ion-implanted silicon during laser annealing

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The time-resolved reflectivity at 0.63 μm from arsenic-implanted silicon crystals has been measured during annealing by a 1.06-μm laser pulse of 50-ns duration. The reflectivity was observed to change abruptly to the value consistent with liquid silicon and to remain at that value for a period of time which ranged from a few tens of nanoseconds to several hundreds of nanoseconds, depending on the annealing pulse intensity. Concurrently, the transmission of the primary annealing beam dropped abruptly. These observations confirm the formation of a metallic liquid phase at the crystal surface during the annealing process.

PACS numbers: 81.40.Tv, 79.20.Ds, 61.70.Wp, 61.70.Tm

Illumination by high-power lasers has been demonstrated to be an effective method of annealing ion implantation damage in semiconductors.[1] In spite of considerable activity devoted to various applications of this technique, the basic physical mechanisms for the annealing have not been clarified. It has been suggested that under certain conditions the amorphous layer may melt and regrow epitaxially.[2] Conclusive experimental evidence in support of this hypothesis has, however, not been presented. In this letter we report time-resolved measurements of the reflectivity of the semiconductor surface which confirm that, in the laser annealing process, single-crystal regrowth occurs from a melted surface layer. Measurements of the duration of the liquid layer as a function of laser energy are also presented.

The samples used in these experiments were 0.25-mm-thick (111) silicon wafers cut from a 1000-Ω cm *p*-type dislocation-free floating-zone ingot. They were polished with syton on both faces to permit the observation of the transmitted annealing laser beam. Arsenic ions were implanted at an energy of 50 keV on one sur-

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face of each crystal. The doses of implanted ions ranged from $10^{14}$ to $10^{17}/\mathrm{cm}^2$. Rutherford backscattering spectra showed an impurity profile which peaked at 320 Å from the surface with a $1/e$ halfwidth of 170 Å.

A Q-switched Nd: glass oscillator and amplifier system was used to generate the annealing pulses at a wavelength of 1.06 μm. Mode control was used in the oscillator to produce a single transverse mode having a Gaussian profile and a diameter (FWHM) of 1.2 mm at the oscillator output and 3.3 mm at the samples. The duration of the pulses was 50 ns (FWHM). By varying the gain of the optical amplifier it was possible to continuously adjust the incident annealing pulse energy from 0.65 to 16 $\mathrm{J/cm}^2$ and the corresponding peak intensity from 12 to 300 $\mathrm{MW/cm}^2$. In the data reported here each laser pulse was incident on a portion of the sample not previously exposed to the laser beam. Both the incident and transmitted 1.06-μm pulses were recorded with high-speed photodiodes and oscilloscopes with response times of 1 ns. A small (1-mm) aperture was placed behind the sample to ensure that only the central portion of the transmitted beam was measured.

A continuous 0.63-μm He-Ne laser was used to measure the optical reflectivity of the implanted surface during the annealing. This beam was focused to a diameter of approximately 0.3 mm and was aligned with the center of the annealing beam at the crystal surface. The angle of incidence of the 0.63-μm beam was 57.5° to the surface normal. A polarizer and quarter-wave plate were employed to measure the reflectivity for both perpendicular and parallel polarizations, $R_\perp$ and $R_\parallel$, respectively. An avalanche silicon photodiode was used to detect the reflected beam with a risetime of approximately 3 ns. Accurate timing was ensured by synchronously triggering the recording of the incident and transmitted 1.06-μm pulses and the 0.63-μm reflectivity signal.

The extent of the annealing in the samples was determined by Rutherford backscattering and channeling analysis using 1.9 MeV $He^+$ ions. For example, at an incident laser energy of 4 $\mathrm{J/cm}^2$ on the $10^{16}/\mathrm{cm}^2$ sample, the channeled spectrum of the annealed sample had a minimum yield of approximately 3% for both the

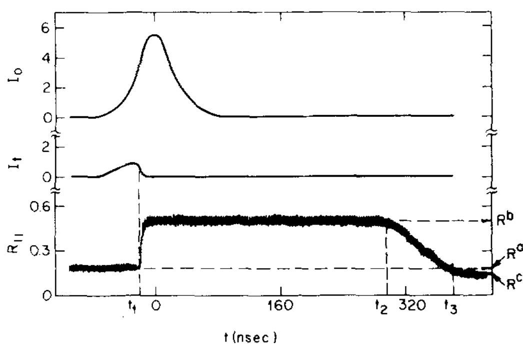


FIG. 1. Shown as a function of time are $I_0$, the incident laser intensity at 1.06 μm, $I_t$, the transmitted laser intensity (in arbitrary units), and $R_\parallel$, which is the absolute value of the reflectivity at 0.63 μm for light polarized parallel to the plane of incidence. The incident energy was 5.2 $\mathrm{J/cm}^2$ and the implant dose was $10^{15}/\mathrm{cm}^2$.

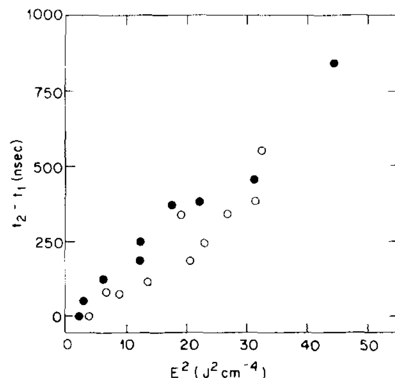


FIG. 2. The duration of the reflectivity flat top, $t_2 - t_1$, is shown as a function of the square of the incident laser energy per unit area, $E$. The open and dark circles are the experimental data for $10^{15}$ and $10^{16}$ As ions/$\mathrm{cm}^2$ samples, respectively.

Si and As spectra. This value is comparable to that of unimplanted single-crystal Si. Furthermore, it indicates that the complex and extended damage associated with ion implantation has been annealed and that the As has been completely incorporated into substitutional lattice sites. The threshold for annealing was estimated to be 3 $\mathrm{J/cm}^2$ for an ion dose of $10^{16}/\mathrm{cm}^2$. After annealing with the highest-energy pulses the concentration of As atoms fell to $1/e$ of its maximum value at a depth of 2000 Å.

The time-resolved reflectivity measurements are illustrated in Fig. 1. These waveforms have a number of distinguishing features which constitute a characteristic "signature" for laser annealing. At a time $t_1$ a sharp transition occurred when the transmitted 1.06-μm intensity decreased abruptly and simultaneously the reflectivity of the 0.63-μm beam increased from an initial value $R^a$ to a new value $R^b$. This enhanced reflectivity remained constant until time $t_2$ when it decreased to a new steady-state value $R^c$ at time $t_3$. For the $10^{16}/\mathrm{cm}^2$ sample, $R_\parallel^a$, $R_\parallel^b$, and $R_\parallel^c$ were measured to be 0.17, 0.47, and 0.13, respectively, and $R_\perp^a$, $R_\perp^b$, and $R_\perp^c$ were 0.63, 0.82, and 0.57, respectively. These values agree to within ±10% with the calculated reflectivities of amorphous metallic liquid[3] and crystalline silicon, respectively. The measured values did not change with increasing pulse energy and varied only slightly for different implant doses. Below energies of 1.6 $\mathrm{J/cm}^2$ for the $10^{16}/\mathrm{cm}^2$ (2.2 $\mathrm{J/cm}^2$ for $10^{15}/\mathrm{cm}^2$) no appreciable change in reflectivity was observed. As the pulse energy was increased above these values, the duration of the flat portion increased, reaching a maximum of as much as 800 ns. This is illustrated in Fig. 2, where the duration, $t_2 - t_1$, of the flat portion of the reflectivity waveform is plotted as a function of the square of the incident pulse energy per unit area, $E$. The threshold for catastrophic surface damage was approximately 7 $\mathrm{J/cm}^2$ for both $10^{15}$ and $10^{16}/\mathrm{cm}^2$ samples.

The onset of the reflectivity change at time $t_1$ was observed to move back towards the leading edge of the incident pulse as the pulse energy increased. The integrated energy of the incident laser pulse from the



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beginning of the pulse to time $t_1$ was found to be nearly constant for a given sample over the measured range of total pulse energies and found to be $0.9 \pm 0.1$ and $1.3 \pm 0.05$ J/cm$^2$ for $10^{16}$- and $10^{15}$-ions/cm$^2$ samples, respectively.

As previously stated, the reflectivities $R_{\parallel}^b$ and $R_{\perp}^b$ are consistent with the measured values of the complex index of refraction of liquid silicon[3] (i.e., $n=2.9$ and $k=5.1$ at $\lambda=0.63$ $\mu$m). If the liquid Si were less than 200 Å thick, the observed values of reflectivity at 0.63 $\mu$m would differ measurably from those predicted for an infinitely thick liquid. At 1.06 $\mu$m the extinction length $(\lambda/4\pi k)$ in liquid Si is 120 Å, which accounts for the abrupt decrease in transmission of the annealing beam at time $t_1$ when the surface melts. The constant value of the reflectivity between $t_1$ and $t_2$ is strong evidence that the surface remains a liquid during this time interval. After $t_1$, the absorption of the annealing beam is determined entirely by the optical properties of the liquid and the laser energy is deposited at a thin layer at the surface.

During the 50-ns laser pulse, heat will diffuse into the solid approximately 2 $\mu$m. Above the threshold energy for the observed reflectivity increase, the absorbed energy cannot all be stored in this thickness of hot solid and must cause melting at the surface. For the longest observed flat-top reflectivity waveform, we estimate the thickness of this liquid layer to be 1 $\mu$m. This distance is longer than the final depth of the As atoms. If we assume the As moves in the liquid by diffusion, then the penetration depth will be approximately $(2D_L\tau)^{1/2}$, where $\tau$ is the difference between $t_2$ and $t_1$ and $D_L$, the diffusion coefficient of As in liquid silicon, is estimated[4] to be $1\times10^{-4}$ cm$^2$ s$^{-1}$. The As will then diffuse approximately 1300 Å. Since the initial distribution was peaked at 320 Å, the final distribution would be expected to be $1/e$ of its maximum experimental value at approximately 1600 Å, in reasonable agreement with the observed diffusion distance of 2000 Å.

The duration of the "flat-top" portion of the reflectivity waveform represents the total time that the surface is a liquid. A rough estimate of this time, $\tau = t_2 - t_1$, can be made in the following way. At time $t_2$, no liquid remains, and the absorbed laser energy is stored in the heat capacity of the hot solid and is distributed over a distance of approximately $E_a C^{-1}(T_m - T_0)^{-1}$, where $E_a$ is the absorbed energy per unit area, $C$ is the heat capacity, and $T_m$ and $T_0$ are the melting and ambient temperatures, respectively. Since the flow of heat is governed by diffusion, this distance is approximately equal to $(2D\tau)^{1/2}$, where $D$ is the thermal diffusivity[5] averaged over the temperature profile (we estimate $D \simeq 0.2$ cm$^2$/s). We find

$$\tau \approx \frac{E_a^2}{(T_m - T_0)^2 C^2 D}. \qquad (1)$$

For values of $E$ large compared to the threshold for melting, $E_a$ is expected to be proportional to $E$. Taking into account the reflectivity of the liquid surface at 1.06 $\mu$m, $E_a \simeq 0.23E$. In this limit of large $E$, expression (1) predicts the experimentally observed quadratic variation of $\tau$ on pulse energy $E$. The magnitude of $\tau$ predicted by Eq. (1) also gives fair agreement with observed results. For example, using $D=0.2$ cm$^2$/s, $C=2.1$ J/cm$^3$ °K, and $T_m=1685$ °K, we find $\tau \simeq 900$ ns for $E=5.5$ J/cm$^2$, compared to the experimental value of 500 ns.

As shown in Fig. 2, the values of $\tau$ for the same laser energies were somewhat larger for the $10^{16}$/cm$^2$ sample than for the $10^{15}$/cm$^2$ sample. One effect which may contribute to this is the increased depth of implantation damage[6] for heavier implant doses which causes the heavier-dose sample to absorb the laser energy more efficiently prior to melting than the lighter-dose sample. Further studies elucidating the details of the annealing dynamics prior to melting are planned.

In the experiments reported here, we have presented conclusive evidence for the melting of the surface of ion-implanted semiconductors during laser annealing. The liquid layer lasts for tens to hundreds of nanoseconds and has an approximately quadratic variation with absorbed laser energy. A model based on diffusion of heat into the solid gives reasonable agreement with these observations. In addition to arsenic-implanted silicon we have also observed similar reflectivity signatures from Te implanted in GaAs, Te and N in GaP, Te in InP, amorphous silicon on silicon, as well as single-crystal silicon and germanium.

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# Hydrogenation of evaporated amorphous silicon films by plasma treatment

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It is shown that heat treatment in a hydrogen plasma of pure amorphous silicon films prepared by UHV evaporation yields a material with no observable dangling bond ESR signal. This material has electrical properties similar to films prepared by a glow-discharge decomposition of silane but a lower hydrogen content as deduced from ir absorption data.

PACS numbers: 68.55.+b, 81.15.Ef, 81.40.Rs

We report on the preparation and properties of hydrogenated amorphous silicon films obtained by diffusing atomic hydrogen into pure UHV-evaporated material. These experiments have been performed both as a new technique to obtain material suitable for devices and as a means to investigate the role hydrogen plays in *a*-Si prepared by other methods such as silane decomposition.

Vacuum deposition of pure amorphous silicon produces films unsuitable for electronic applications because of a large density of defect-related states. At least part of these states can be associated with dangling bonds observable by ESR.[1,2] It has been shown that for deposition under UHV conditions, the minimum density of these dangling bonds is $3\times10^{19}$ $cm^{-3}$,[3] i.e., one for every $10^3$ atoms, irrespective of deposition conditions and subsequent anneals. This is not true, however, when contamination is present during deposition or annealing.[4] On the other hand, films deposited by techniques that imply the presence of atomic hydrogen, such as silane decomposition, can have a much lower density of defect states and be suitable for applications.[5] It is still controversial whether hydrogen has the simple role of chemically saturating dangling bonds, of if, at least in some cases, there are other virtues inherent to the above techniques to eliminate defect states.

The idea of diffusing hydrogen into pure amorphous silicon is an obvious one. It is also clear that this will be more easily achieved using atomic hydrogen than can be produced by plasma decomposition of molecular hydrogen. Indeed, Lecomber *et al.*[6] have reported such an experiment and have shown that the dangling bond ESR signal was eliminated by heat treatment under a hydrogen plasma. The resulting material, however, did not have the high resistivity of silane-produced *a*-Si. The films had been produced by evaporation under conventional vacuum conditions (pressure during evaporation ~ $10^{-6}$ Torr, evaporation rate < 30 Å/s) for which contamination is not negligible, as evidenced by the observed dependence of spin density on evaporation rate. The films used in the present study have been evaporated under ultra-high-vacuum conditions[3,7] (pressure during evaporation < $10^{-8}$ Torr, evaporation rate ~ 30 Å/s). A detailed ESR investigation of these and similar films[3] indicates that the spin density becomes independent of the evaporation rate above a rate of 3 Å/s. In addition, by operating at elevated substrate temperatures ($T > 350\,^\circ$C) one obtains films with a low degree of porosity which are not contaminated upon exposure to air and are stable with respect to subsequent annealing below crystallization temperature.[3] We report that films prepared under these conditions, when treated under a hydrogen plasma, acquire properties similar to that of silane-produced films.

The system for treating films in a hydrogen plasma

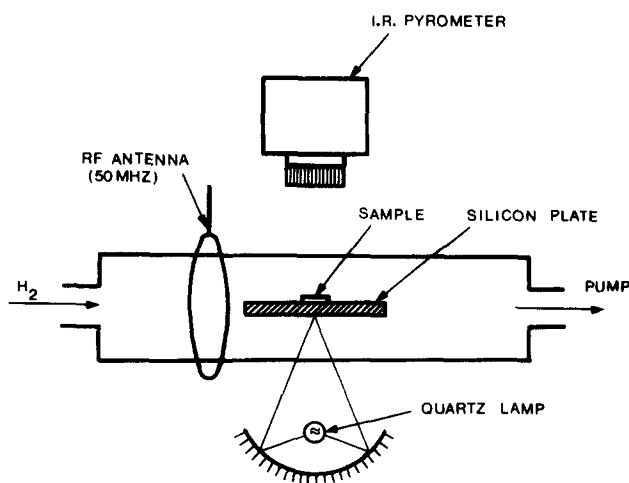


FIG. 1. Plasma treatment setup.

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