Laser Annealing of Damaged Silicon Covered with a Metal Film: Test for Epitaxial Growth from the Melt

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Damage annealing of a silicon wafer covered by a Ti layer has been obtained by irradiation with a ruby-laser 20-ns pulse of 1 J/cm^2 energy density. The thickness of the metal film was chosen so as to ensure complete absorption of the light in order to avoid the formation of a photoexcited electron-hole plasma in Si. The results show a good annealing of the Si damage and a titanium diffusion coefficient consistent with an epitaxial growth from the melt.

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It is well known that a high-crystallographic-quality material can be obtained by short-pulse laser irradiation of heavily damaged silicon samples. However, the mechanism involved in the annealing process is still controversial. Several authors[1-4] claim that annealing occurs through a thermal melting followed by epitaxial recrystallization on the underlying single-crystal substrate.

According to other authors,[5-7] annealing is obtained through a nonthermal process involving the formation of a dense electron-hole plasma, which transfers the excitation energy to the lattice at a slow rate.[8] Because of the excitation of bonding electrons the covalent bond weakens, the crystal structure becomes unable to support shear, and atomic rearrangement occurs through a second-order phase transition. This process has been called "plasma annealing."

While this work was in progress, two experiments which discriminate between the two mechanisms have been published. One is based on the measure of the silicon reflectivity at different wavelengths during laser annealing.[9] The other one is based on the dependence of the annealing energy threshold on the duration of the laser pulse.[10] Both give results consistent with the melting model but inconsistent with the formation of a dense electron-hole plasma.

The present work presents an experiment which can discriminate between the simple thermal process and plasma annealing. The experimental principle is simple: The surface of a silicon sample damaged by ion implantation is covered by a metal film thick enough to absorb all the incident laser radiation. Under these conditions the dense electron-hole plasma in the semiconductor cannot be photoexcited by laser irradiation. As a consequence, if any annealing of the underlying damaged silicon took place after laser irradiation, it could only be due to a thermal energy transfer from the metal to the semiconductor. On the contrary, the absence of annealing in covered silicon under conditions producing annealing in an uncoated sample would mean that a simple thermal process is inadequate.

The experimental problems arise in choosing a suitable metal to overlay the silicon surface. The characteristics of the metal are in fact strictly defined: (i) melting temperature higher than silicon, (ii) very low diffusivity of the metal in silicon, and (iii) reflection coefficient not too different from that of silicon.

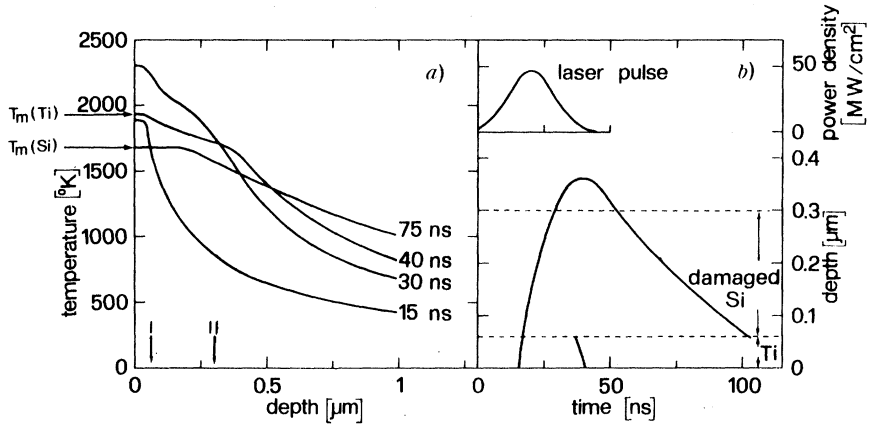

FIG. 1. (a) Calculated time evolution of the temperature profile vs depth for a Gaussian ruby-laser pulse of total energy 1 J/cm^2 and 20 ns FWHM. On the ordinates T_m(Ti) and T_m(Si) are the melting points of titanium and silicon, respectively. The arrows marked with I and II on abscissas represent the end of the titanium film (60 nm) and of the damaged silicon layer (300 nm), respectively. (b) Calculated penetration depth of the melt front vs time under the same conditions as (a). The laser pulse is given for comparison.

Titanium was found to fulfill these conditions. A 62-nm-thick titanium film was deposited on a [100] Si wafer. This thickness is high enough to ensure complete light absorption, as the absorption coefficient of the laser light used is about 5×10^5 cm^{-1} in Ti. The sample was then implanted with a dose of 10^{16} Ne$^+$ ions/cm^2 at an energy of 130 keV. This implantation produces a highly damaged layer ($\chi_{[100]} = 0.8$ for a 2.0-MeV He beam) 150 nm full width at half maximum (FWHM) thick, centered at 165 nm below the silicon surface.

A Q-switched ruby laser with the beam homogenized by the use of a 90° bent-quartz-crystal optical guide has been used for irradiation. Energy densities ranging from 1 to 2 J/cm^2 were chosen to perform the irradiation. The pulse duration was 20 ns. The choice of this energy interval was based on the following considerations. With a spatially inhomogeneous beam, a very good annealing of uncoated silicon, ion implanted at nearly the same conditions, was found to occur at 1.4 J/cm^2.[11] Calculations based on a model[12] of the type used by Baeri *et al.*[1] show that at 1 J/cm^2 the damaged layer of silicon remains molten for about 60 ns. According to this computation, the titanium film should also melt but only for about 20 ns (see Fig. 1). Of course, because of the uncertainties in the optical and thermal parameters introduced, these calculations cannot be taken too literally, so they were used as an indication of the energy interval to be explored in order to find more exactly the conditions under which the titanium film is not torn off.

For energies above 1.5 J/cm^2 the titanium film melts, leaving small spherical drops solidified on the silicon surface [Fig. 2(a)], and a good an-

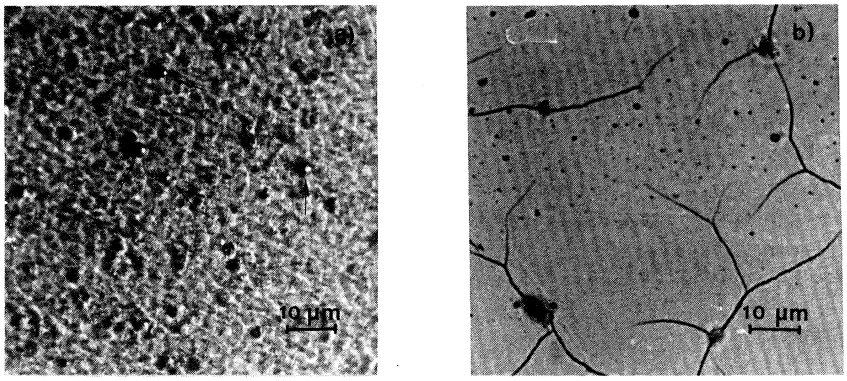

FIG. 2. (a) Photomicrograph of the titanium-covered silicon after a 1.5-J/cm^2, 20-ns ruby-laser pulse. Ti drops, residual of the irradiated film, are shown by arrows. (b) The same after a 1.0-J/cm^2, 20-ns pulse.

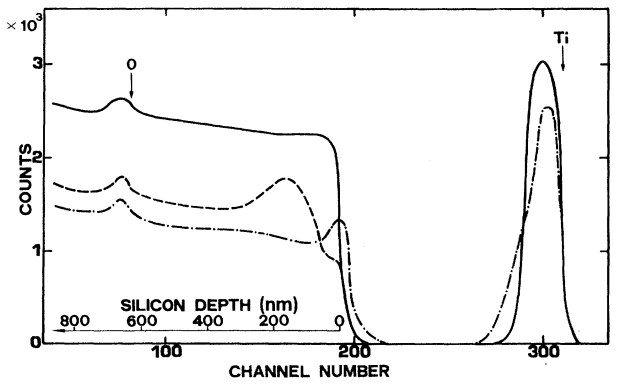

FIG. 3. 1.8-MeV He^+ backscattering spectra obtained from titanium-covered [100] silicon. Solid and dashed lines, random and aligned spectra, respectively, before laser irradiation (these curves superimpose for the Ti signal); dot-dashed line, aligned spectrum after a 1-J/cm^2, 20-ns ruby-laser pulse. The arrow marked O shows the expected position of the signal due to oxygen lying at the Ti surface.

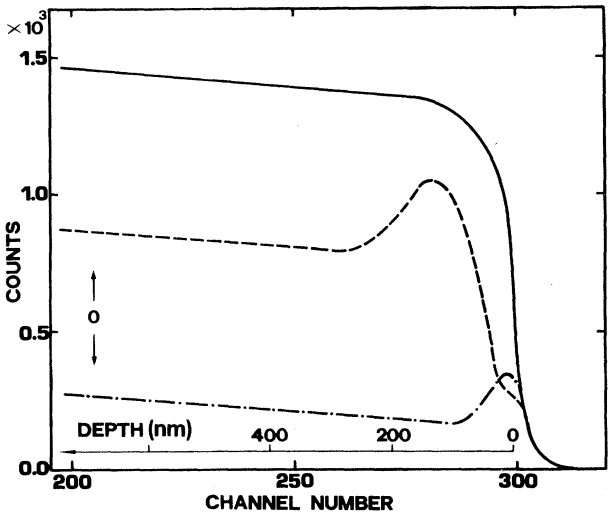

FIG. 4. 2-MeV He^+ backscattering spectra obtained after the removal of the titanium film from the sample of Fig. 3. The symbols have the same meaning as in Fig. 3.

nealing of the underlying silicon is achieved. However, because of the disappearance of the titanium-film continuity in the course of irradiation, the laser light may have reached the silicon substrate, and the formation of an electron-hole plasma cannot be excluded.

By lowering the energy density of the laser pulse down to 1 J/cm^2, a more suitable condition can be achieved. In fact, as it can be seen in Fig. 2(b), at this energy only some cracks are formed on part of the film. This indicates either that the titanium film does not melt or that melting does not last long enough to destroy the film continuity. In any case, the laser light cannot reach the underlying silicon.

Rutherford-backscattering spectra with 1.8-MeV He^+ ions were taken inside and outside the region irradiated with a 1-J/cm^2 pulse energy density. Figure 3 shows the random and aligned spectra relative to the different regions of the sample. After the laser irradiation, the implantation damage peak completely disappears and a disorder peak at the Ti-Si interface becomes evident. This disordered layer is connected to the small interdiffusion which is evidenced by the change of the titanium peak shape and by the energy shift of the Si signal. The oxygen appearing in the spectra amounts to about 10^{17} atoms/cm^2, well within the solubility limit in Ti, and is contained in the metal film. This is demonstrated by the absence of oxygen peaks in Fig. 4, which represents aligned and random spectra after the removal of the metal film by using a 4% HF etch. The comparison of Figs. 3 and 4 also shows that the very high minimum yield (50%) of the annealed Ti-covered sample is mainly due to the multiple scattering of the beam in the metal film. The corresponding spectrum in Fig. 4 exhibits a 12% minimum yield. The peak observed at the Ti-Si interface in Fig. 3 is now at the surface. Its integral corresponds to about 6×10^{16} Si atoms/cm^2; this number is indicative of the thickness of the disordered layer formed by interdiffusion.

In conclusion, this experiment shows that the energy necessary to anneal the damaged silicon is not supplied to the atoms via a photoexcited electron-hole plasma. The interpretation of our experiment is that the heat propagation from titanium to silicon leads to the melting of the latter. Further evidence in favor of a melting mechanism is given by the interdiffusion between titanium and silicon, displayed by the backscattering spectra, which involves diffusion coefficients of the order of 10^{-4} cm^2/s typical of the liquid state. Since the dielectric screening of the Coulomb interaction resulting from the dense electron-hole plasma cannot be invoked in our case, enhanced diffusion processes due to the vacancies released by the charged-impurity–vacancy complexes cannot account for such a high diffusion coefficient.

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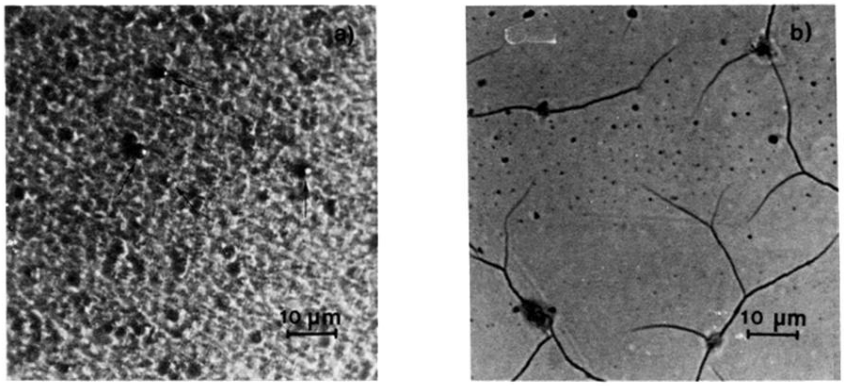

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