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TRANSMISSION ELECTRON MICROSCOPE STUDIES OF LASER AND THERMALLY ANNEALED ION IMPLANTED SILICON*

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ABSTRACT

Transmission electron microscopy has been used to study the effects of high power laser pulses on boron, phosphorous and arsenic implanted <100> silicon crystals. No defects (dislocations, dislocation loops and/or stacking faults) were observed in either as-grown or implanted silicon after one pulse of ruby laser irradiation (λ = 0.694μm, pulse energy density 1.5 - 1.8 J cm^{-2}, 50 x 10^{-9} pulse duration time). The concentration of boron in solution, as inferred from electrical measurements, could exceed the equilibrium solubility. In thermally annealed specimens, on the other hand, significant damage remained even after annealing at 1100°C for 30 minutes. On thermally annealing the implanted, laser-treated specimens, precipitation of the implanted boron ions occurred whenever the implanted doses were in excess of the equilibrium solubility limits. The relationship of these observations to the results of electrical measurements made on these samples will be discussed.

I. INTRODUCTION

High temperature thermal diffusion for p-n junction formation has been replaced in recent years by ion implantation techniques for many device applications, because the characteristics of the junction can be accurately controlled by the dose and the energy of the implanted ions. However, the crystal lattice is damaged by the energetic ions, and most of the dopant ions are not electrically active because they are not in substitutional lattice positions. The conventional method of removing this damage and electrically activating the dopants has been thermal annealing which, unfortunately, has undesirable consequences, such as precipitation of dopants in the implanted layer, degradation of electrical properties such as minority carrier diffusion length and usually only partial removal of the lattice damage in the implanted layer.

It was recently reported[1,2] that a complete annealing of displacement damage in silicon introduced by boron ion implantation can be accomplished by high power laser pulses. The effects of laser annealing can be confined to the ion implanted layer by the proper choice of the wavelength, energy and pulse duration time of the laser. As a result of this, complete electrical activity was recovered and the minority carrier diffusion length in the underlying substrate material was unaffected.

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In this paper, we present further results on the residual damage and electrical characteristics after laser and thermal annealing of boron, phosphorous and arsenic implanted specimens.

II. EXPERIMENTAL PROCEDURE

The silicon single crystals with (100) faces used in this investigation were obtained from Monsanto. Boron ($^{11}B^+$, 35KV) implantations were carried out on 80 Ω-cm, n-type, FZ specimens; phosphorous ($^{31}P^+$, 80KV) and arsenic ($^{75}As^+$, 100KV) implantations were done on 10 Ω-cm, p-type, FZ specimens. The specimens were polished in CP-6 solution. A vacuum of about 2×10^{-8} Torr was maintained in the chamber during the implantation. The doses of implanted ions varied from 10^{14} - 2×10^{16} ions cm^{-2}. Following the implantation, the specimens at each dose were halved for subsequent laser and thermal annealing treatments. Laser annealing was accomplished by using the Q-switched output of a ruby laser (λ = 0.694μm, pulse duration time ~50×10^{-9} sec) with an energy density of 1.5 - 1.8 J cm^{-2} per pulse. This energy density was found to be greater than the threshold (~1.3 J cm^{-2}) required to anneal the implanted damage. All the work presented here was done using one pulse of the laser. Thermal annealing was performed in a quartz furnace under helium gas-flow. Electrical property measurements were made using Hall effect and surface photovoltage (SPV) measurements on the same samples which were used for electron microscopy.

III. RESULTS AND DISCUSSION

Fig. 1a is a micrograph of a specimen which was laser treated after the boron implantation dose of 3×10^{15} cm^{-2}. In this micrograph, no defects in any form (dislocation loops, precipitates, stacking faults and subgrain boundaries) are observed down to the microscope resolution of ~10A°. Fig. 1b is a diffraction pattern of the implanted-laser treated specimen, showing that the implanted layer has the same orientation [001] as the substrate; no irregularity of the diffraction pattern is also an indication of the perfection of the lattice. Similar results were obtained for laser treated specimens which were implanted up to doses of 2×10^{16} cm^{-2}. In the implanted specimens which were subsequently thermally annealed, a considerable amount of damage remained even after annealing at 1100°C. Examples are shown in Fig. 1b and 1c for specimens (dose = 3×10^{15} cm^{-2}) annealed at 900°C and 1100°C for 30 min. respectively. After annealing at 900°C, a high concentration of dislocation loops (loop density ~1.0×10^{16} cm^{-3}, average size = 250 Å), was observed. The nature of large loops (>150Å) was analysed using the inside-outside contrast method and they were found to be interstitial type. The nature of the small loops (<150Å) is currently being investigated and the results will be reported at a later date. Most of the larger loops have a/2<110> Burgers vectors with a small density (~2×10^{14} cm^{-3}) of a/3<111> faulted loops (see the loops containing the fault fringes). In the samples which were annealed to 1100°C for 30 minutes, a network of dislocations of a/2<110> Burgers vectors was observed. The number density of both perfect and faulted loops decreased to 2 x 10^{12} cm^{-3} (average size 800 Å) and 6 x 10^{11} (average size 8000 Å) respectively. It should be noted that rod-shaped defects (presumably boron precipitates), which have been reported in the boron irradiated specimens after annealing around 800°C, were not observed in the present studies after annealing at 900°C or above.[3]

The observed annealing of defects in laser and thermally treated specimens is reflected in the electrically active carrier concentration. Fig. 2 is a plot of measured carrier concentration as a function of implanted dose of boron ions. The solid curve represents a complete electrical recovery for the implanted ions. Partial electrical recovery for the thermally annealed specimens is in qualitative agreement with the residual damage. The excess carrier concentration over the implanted dose for the case of laser treated specimens is unexpected; it cannot be explained by the nonuniform distribution of densities and mobilities in the implanted layer. This point is currently under investigation.

A comparison between the laser and thermal annealing for the case of phosphorous implanted silicon is shown in Fig. 3. Again no damage was observed in the implanted (dose = 1.0 x 10^{15} cm^{-2}), laser treated specimens (Fig. 3a) whereas in implanted, thermally annealed (1100°C for 30 min) specimens, residual damage in the form of dislocation loops was observed (Fig. 3b). An average loop size of 300 Å and a number density of 4.0 x 10^{14} cm^{-3} were found. Electrical measurements on the implanted-laser treated specimens showed a complete recovery to slightly higher than the implanted dose and in the thermally annealed specimens only a partial recovery of carrier concentration was realized.

Similarly, in the arsenic implanted (dose = 1.0 x 10^{16} cm^{-2}) specimens, no damage was observed after the laser annealing, as shown in Fig. 4a, but in the implanted thermally annealed (600°C for 30 min) specimens, dislocation loops with an average size of 43 Å and number density of 4.5 x 10^{16} cm^{-3}, were observed. Fig. 5 shows the measured carrier concentration as a function of implanted dose. The laser treated specimens show complete recovery of electrical activity of the implanted ions, whereas thermally annealed specimens show only partial recovery.

Since the electron microscope resolution for defect clusters is about 10 Å, the question arose as to whether or not there are point defects or small clusters thereof, not visible in the microscope. To investigate this, the laser-treated specimens were subsequently annealed at high temperatures (600°C and 900°C for 30 min) and thinned to study by electronmicroscopy, the clustering of defects and/or precipitation of boron. As discussed by Frank, all point defects in silicon should be mobile by 900°C. No clusters or defects in any form were observed after annealing either at 600°C or at 900°C in the specimens which were implanted with doses less than the equilibrium solubility limit. Electrical measurements on these specimens showed no changes in carrier concentrations either after 600°C or after 900°C annealing. In the specimens, where the implanted dose was greater than the solubility limit (solubility limit for 35 KV $^{11}B^{+} \cong 5 \times 10^{15}$ ions cm^{-2}), the precipitation of boron occurred as shown in Fig. 6; here the implanted dose of boron ions was 2×10^{16} cm^{-2}. The precipitation started at 600°C and increased with temperature at 900°C. Electrical measurements showed a small drop in carrier concentration after annealing at 600°C and about 50% drop in carrier concentration after 900°C annealing treatment. From the average precipitate size (65 Å) and number density (2.0×10^{16} cm^{-3}), it can be shown that the decrease in carrier concentration corresponds to the number of boron atoms in the precipitates. The annealing results on the laser treated specimens tend to support that the concentrations of remaining defects, if any, should be very small ($\leq 10^{17}$ cm^{-3}).

In conclusion, it has been shown that the displacement damage produced by the implanted ions in silicon can be removed completely by pulsed laser annealing. A complete electrical recovery of implanted silicon without adversely affecting the minority carrier diffusion length (see the companion paper[4]) is achieved. It is also possible to exceed the equilibrium solid solubility by the laser annealing treatment.

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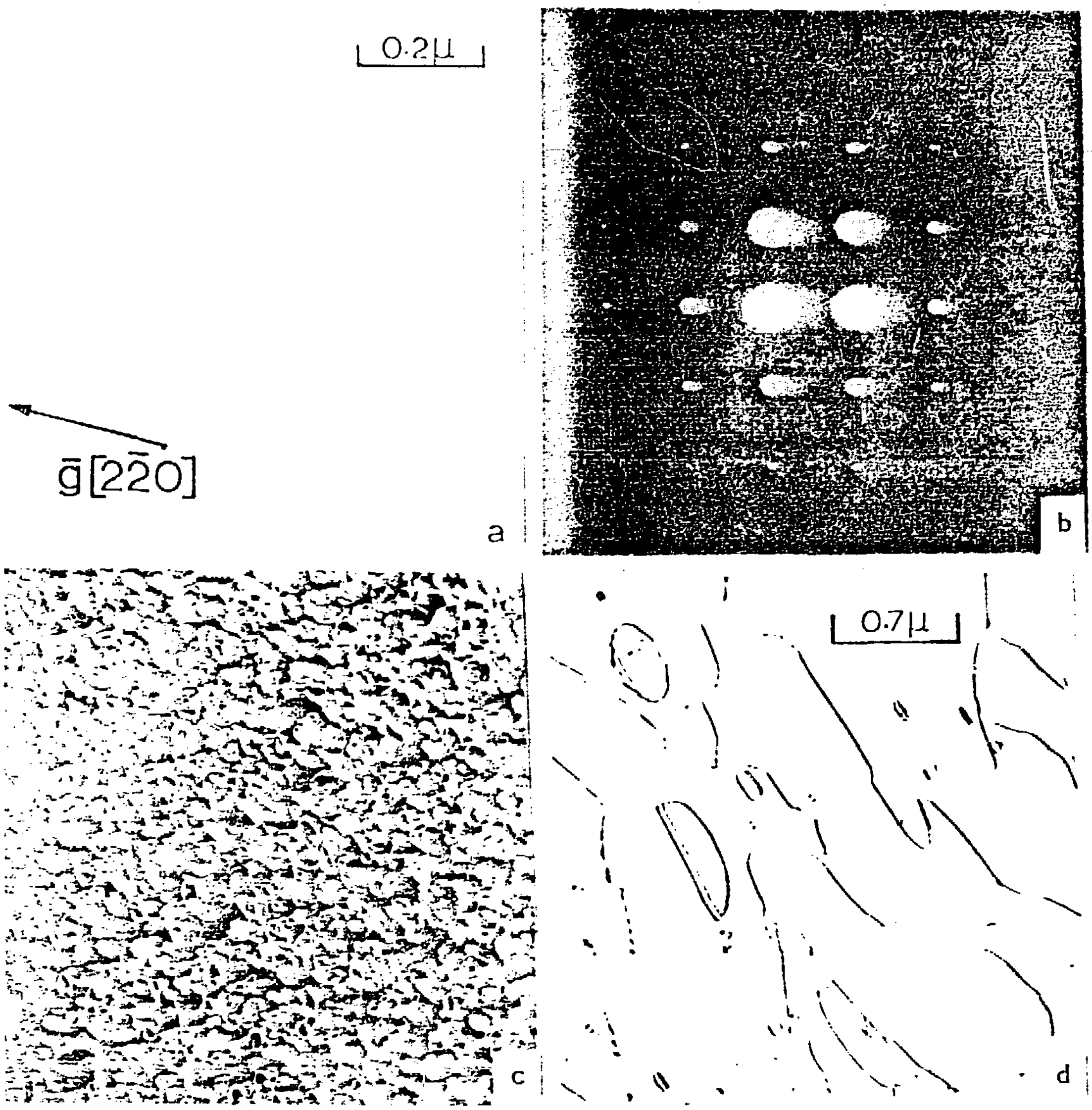

Fig. 1. Comparison of laser and thermal annealing in boron implanted silicon: a) Bright field electron micrograph of implanted ($^{11}B^{+}$, 35 KV, 3 x 10^{15} cm^{-2}) specimens after the laser treatment, b) (001) diffraction pattern of silicon, c) Weak beam dark field electron micrograph of implanted, thermally annealed (900°C, 30 min) specimens, d) Bright field electron micrograph after annealing the implanted specimen at 1100°C for 30 min.

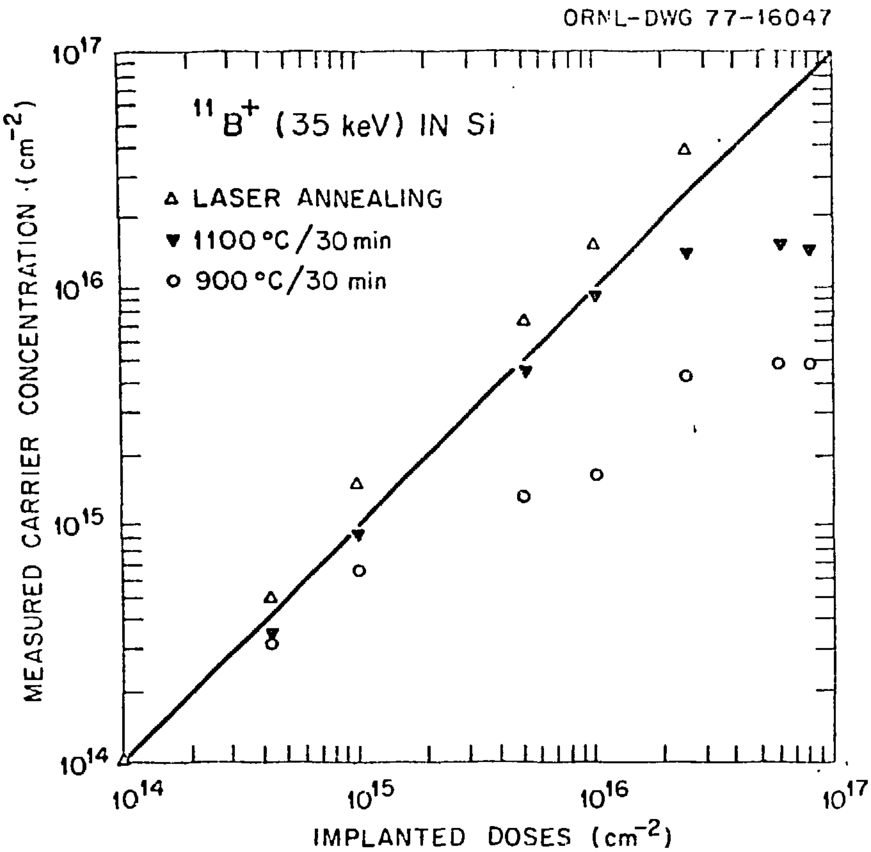

Fig. 2. Measured carrier concentration as a function of implanted dose of boron ions after laser annealing and thermal annealing at 900 or 1100°C for 30 min.

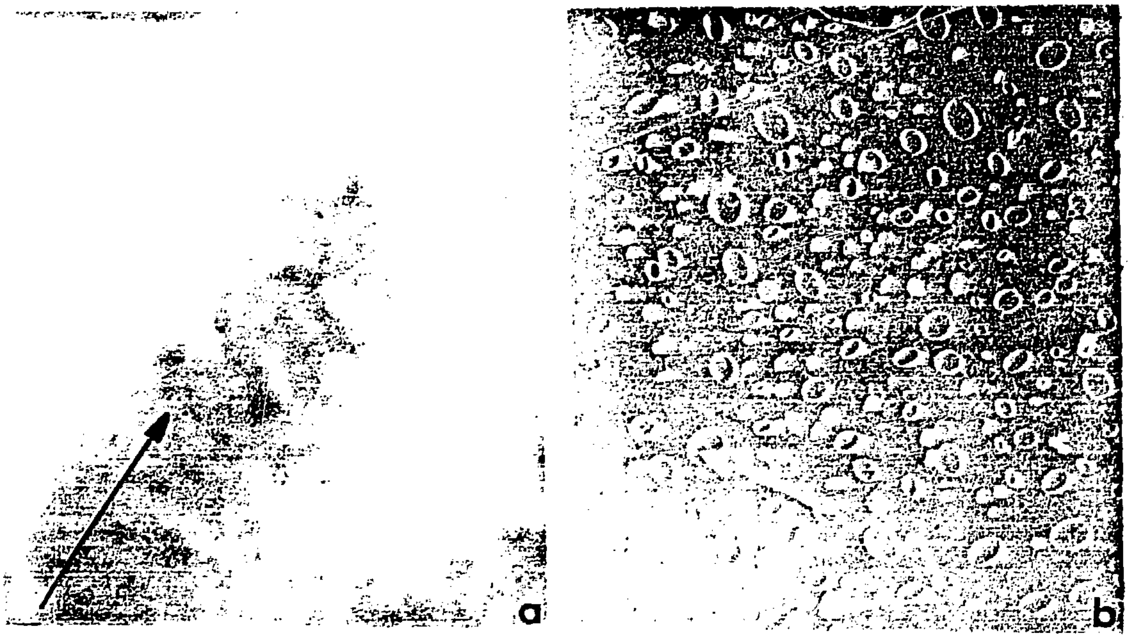

Fig. 3. Comparison of laser and thermal annealing in $^{31}P^+$ implanted (80 KV, dose 1.0 x 10^{15} cm^{-2}) silicon: a) Laser annealed, bright field; b) Weak beam electron micrograph after annealing at 1100°C for 30 min. The arrows indicate the directions of diffraction vector [2$\bar{2}$0] and their length is 0.3μm.

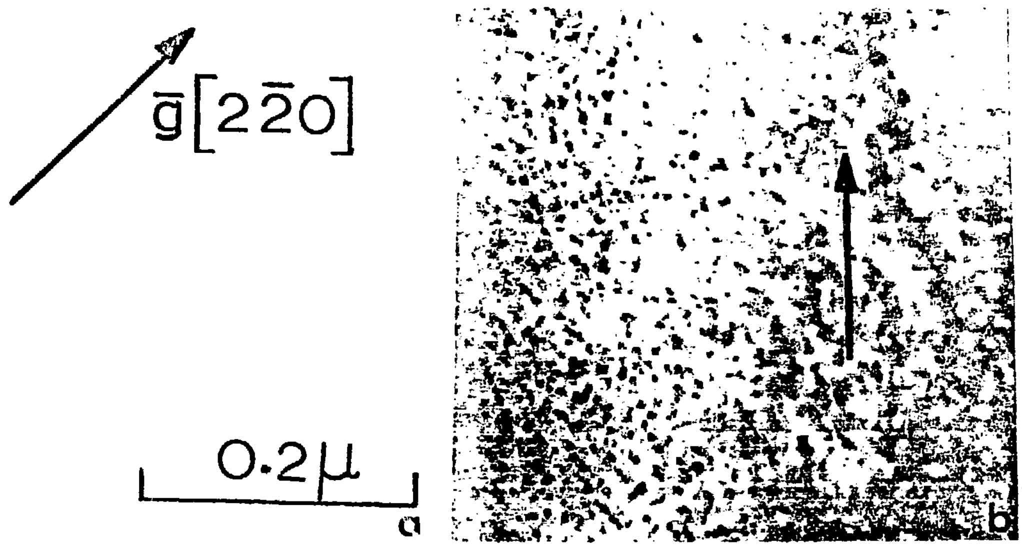

Fig. 4. Comparison of laser and thermal annealing in arsenic ($^{75}As^{+}$) implanted (100KV, dose = 1.0×10^{16} cm^{-2}) silicon: a) Laser annealed, bright field; b) Thermally annealed at 600°C for 30 min, bright field;black-white contrast of defect clusters under dynamical diffraction conditions in this micrograph is characteristic of dislocation loops. The arrows in the micrographs indicate the directions of diffraction vectors [2$\bar{2}$0] and their length 0.2μm.

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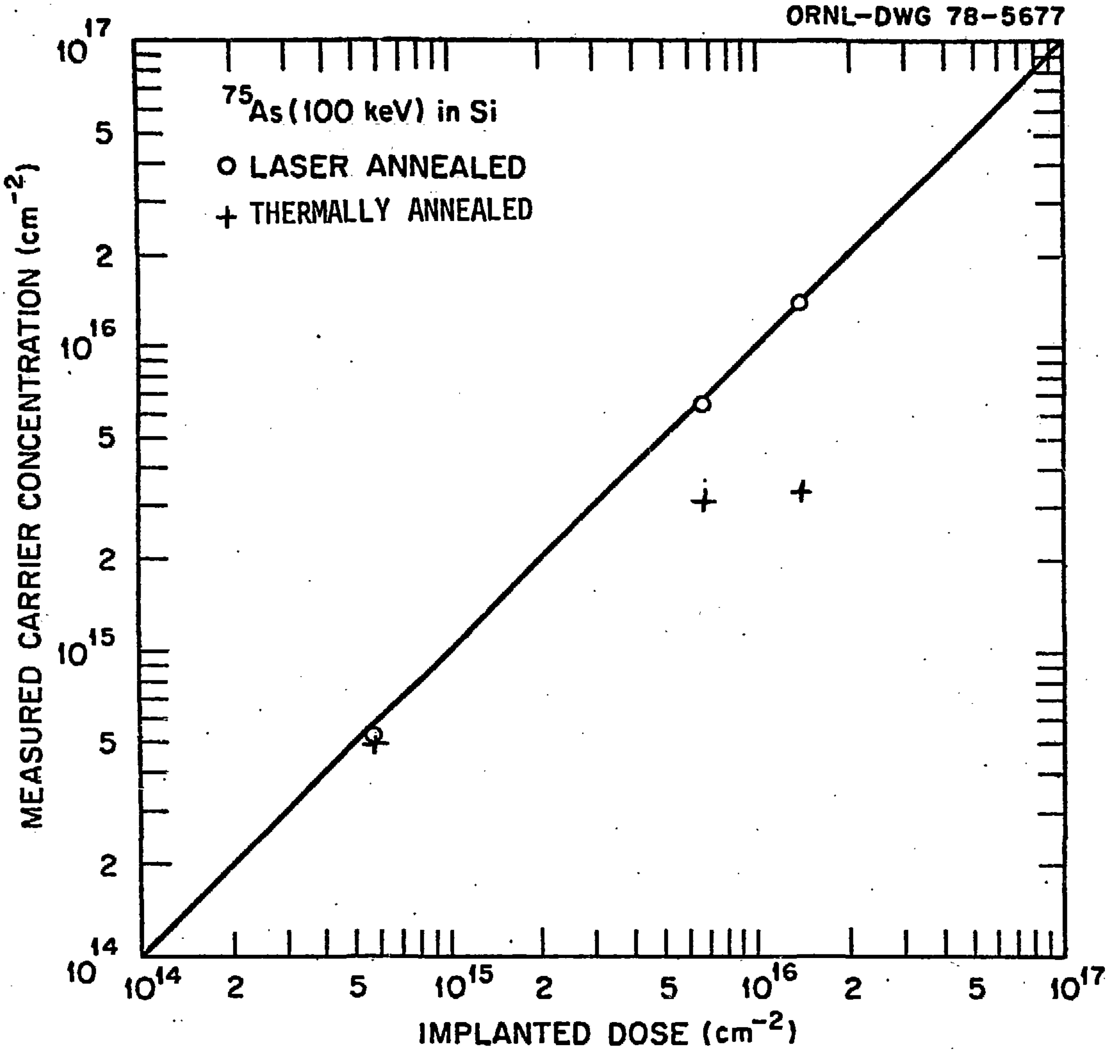

Fig. 5. Measured carrier concentration as a function of implanted dose.

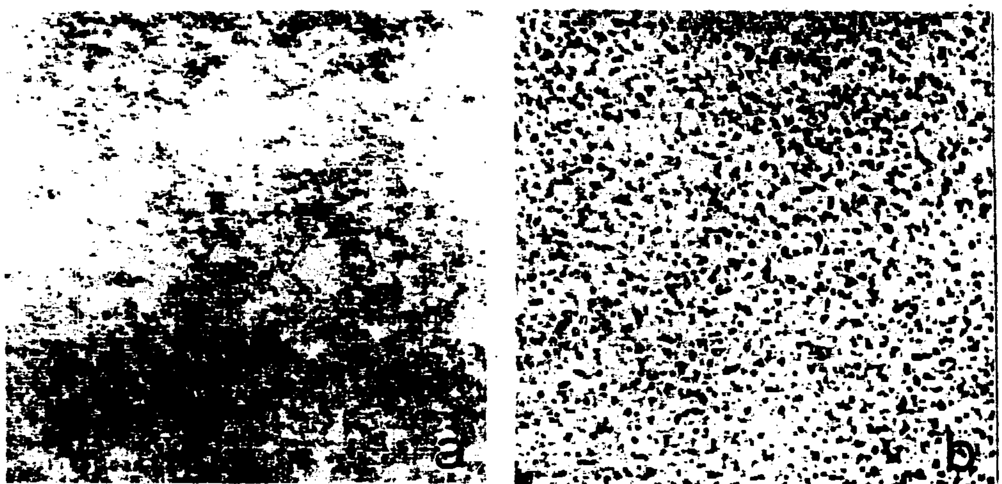

Fig. 6. Boron precipitation in implanted (35KV $^{11}B^{+}$, dose = 2.0×10^{16} cm^{-2}), laser treated specimens: a) Bright field electron micrograph after annealing at 600°C for 30 min., b) Bright field electron micrograph after annealing at 900°C for 30 min. The arrows indicate the directions of diffraction vectors [220] and their length is 0.3μm.