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ION IMPLANTATION OF IMPURITIES INTO POLYCRYSTALLINE SILICON

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Some aspects of concentration profiles and annealing behavior of boron, aluminium, phosphorus, arsenic and indium implanted in polycrystalline silicon films have been studied and compared with those implanted in single crystalline silicon. The obtained results were: (*i*) In isochronal annealing, the electrical sheet resistivity of the implanted poly-Si films decreased abruptly with annealing at about 500°C, and changed its values from minimum to maximum between 600°C and 850°C. (*ii*) The carrier mobility and the carrier electrical activity ratio increased with the implantation dose between 10^{14} to 10^{16} ions/cm^2. (*iii*) The location of peak concentration in boron and phosphorus implanted films annealed at 600°C was in good agreement for single and polycrystalline silicon and bore resemblance to the theoretical profile. (*iv*) Heat treatment at 700°C after implantation produced the movement of impurity atoms towards the surface and into the substrate. In the boron and phosphorus implanted poly-Si films annealed at 1000°C the carrier concentration and mobility were found to be uniformly distributed in the film. (*v*) Only a very small fraction of the aluminium atoms were electrically active between room temperature and 1000°C.

1. *Introduction*

Over the past few years ion implantation has proved to be a powerful method for introducing electrically active dopants into semiconductors. Information on the concentration profile and electrical properties of implanted dopants in semiconductors is important fabrication. As the production of electronic components becomes more sophisticated, there is a need to understand the penetration of ions and the annealing behaviours of dopants not only in monocrystals but also in polycrystalline materials.

A polycrystalline material is composed of small crystallites joined at the grain boundaries. Inside each crystalline the atoms are arranged in a periodic manner so that it can be considered as a small single crystal. The grain boundary usually contains a few atomic layers of disordered atoms which cause the electrical behaviour of a single crystal and polycrystalline semiconductor to differ.

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The polycrystalline silicon is currently used in silicon integrated devices. The use of poly-Si in silicon gate MOS structures is especially important [1]. There have been a few reports on the behaviour of impurities ion-implanted into polycrystalline films [2–5]. They are, however, insufficient to make the electrical characteristics of polysilicon fully understood because physical properties and therefore electrical properties are much influenced by formation and doping conditions. The application of ion implantation for polysilicon as a doping method can separate these complicated relations such as polysilicon film formation, doping and heat treatment.

In this paper, concentration profiles and annealing behaviour of various atoms of impurities implanted into polycrystalline silicon films deposited in a nitrogen atmosphere were studied and compared with those in single crystalline silicon.

2. *Experimental procedure*

The aim of our investigations was to follow up the electrical activity of boron, aluminium, indium, phosphorus and arsenic implanted into polycrystalline silicon films from room temperature up to 1000°C, for fluences ranging between 10^{14} and 10^{17} ions/cm^2. The investigation was performed with polycrystalline silicon films of thickness ranging from 0.5 to 0.6 μm which were deposited on thermally grown SiO_2 with the thickness of 0.135 μm in nitrogen atmosphere at 600°C.

The electromagnetic isotope separator was used to implant ions into freshly polished surfaces of polycrystalline films and single crystal silicon disks, tilted 7° from the $\langle 111 \rangle$ direction to minimize channelling effects. The implantations were performed at room temperature with ions of an energy between 30 and 90 keV. The isochronal annealing was done in an argon atmosphere for 30 and 120 minutes. After each anneal step the electrical sheet resistivity and the conductivity type of implanted surfaces were measured.

The measurement of concentration profiles of phosphorus and arsenic doped polysilicon films were made by a combination of sheet resistivity and the ion etching removal technique described in details in paper [6]. The profiles of the carrier density in boron implanted polysilicon films and single silicon crystals were obtained by combining the Hall effect and sheet resistivity measurements with successive layer stripping.

3. *Effects of annealing temperature on the sheet resistivity*

The implantations of boron atoms were performed at 40, 50, 60, and 70 keV for doses ranging between 10^{14} and 10^{15} ions/cm^2. In Fig. 1 the electrical sheet resistivity for 50 keV boron implanted samples is plotted as a function of the isochronal annealing temperature. The results for other energy implantations are very similar to those shown in Fig. 1. The annealing characteristics of boron implanted polycrystalline films can be subdivided into several regions. For low dose implantation, the sheet resistivity decreased between 500°C and 700°C and changed its values from a minimum to a maximum around 800°C and 900°C, respectively. For higher doses, the sheet resistivity decreased abruptly at 500°C and changed its values from a minimum to a maximum at 600°C and 750°C, respectively.

The sheet resistivity of boron implanted monocrystal silicon as a function of the isochronal annealing temperature is given in Fig. 1 for comparison. These annealing characteristics have three stages: a steady annealing between 300°C and 450°C, a reverse annealing effect between 550°C and 650°C, and lastly, a steady annealing above 700°C. It can be seen that the increase of sheet resistivity, i.e. the so-called reverse annealing, is observed at the temperatures between 550°C and 650°C.

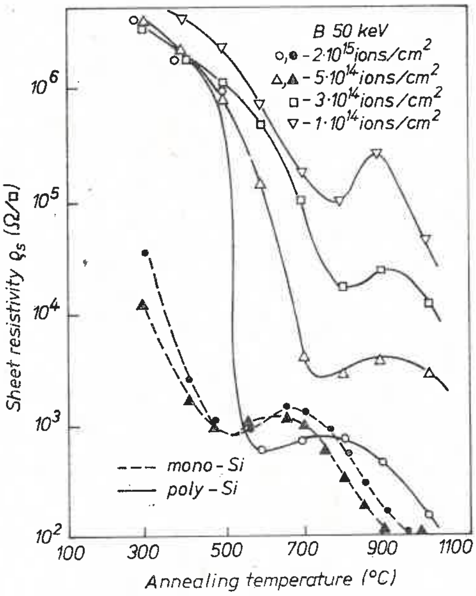

Fig. 1. Variation of sheet resistivity with temperature for a number of boron implantations. Details of the implantations are given in the figure

In Fig. 2 the electrical sheet resistivity of three aluminium doses as a function of the annealing temperature is shown. The implantations were performed at 50 kV energy with doses ranging between 10^{15} and 10^{17} ions/cm^2 at room temperature. For all dose implantations the electrical activity of polycrystalline films increases abruptly at 450°C, and changes its values from a maximum to a minimum around 600°C and 850°C, respectively.

The relation between annealing temperature and sheet resistivity of eight indium doses was measured. The indium implantations were performed at 45 keV and 90 keV energy with doses ranging between 10^{14} and 10^{15} ions/cm^2 (Fig. 3.). In this dose range, the layers will be completely amorphous after the implantation. In all cases, the experimental conductivity of indium implanted polysilicon remained very small compared to the conductivity of single crystalline silicon implanted under this regime [13]. The sheet resistivity did not decrease until the annealing temperature reached 900°C.

The annealing behaviour and electrical activity of arsenic atoms implanted at 30, 45, 50 and 60 keV have been studied between room temperature and 700°C. The annealing characteristics obtained are given in Fig. 3. They agree reasonably well with the experi-

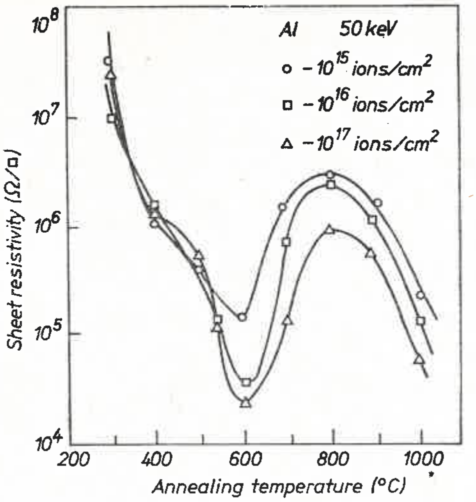

Fig. 2. Temperature dependence of the sheet resistivity of aluminium implanted polycrystalline silicon films. Details of the implantations are given in the figure

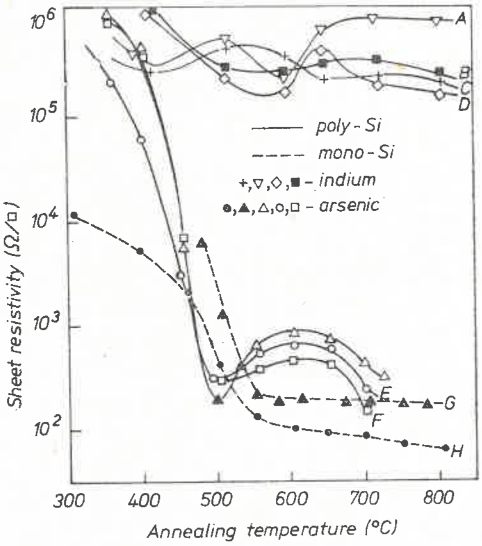

Fig. 3. Variation of the sheet resistivity with annealing temperature for a number of arsenic and indium implantations. Poly-Si films: *A* — 90 keV, 10^{15} In/cm^2; *B* — 45 keV, 10^{14} In/cm^2; *C* — 45 keV, 10^{15} Im/cm^2; *D* — 50 keV, 10^{17} As/cm^2; *E* — 50 keV, 10^{16} As/cm^2; *F* — 50 keV, 10^{15} As/cm^2. Single crystalline Si: *G* — 60 keV, 10^{15} As/cm^2; *H* — 60 keV, 5×10^{15} As/cm^2

mental values measured in a monocrystal implanted under the same conditions. The annealing behaviour of implanted arsenic is not dependent on the implantation energy and can be divided into four regions: a weak annealing from room temperature to 300°C, a steady recovery between 300 and 500°C, a reverse annealing effect between 500 and 600°C and, lastly, a steady annealing above 600°C. The increase of sheet resistivity is observed for the similar temperature range in boron implanted monocrystal silicon.

A typical reverse annealing stage observed in polycrystalline silicon films implanted with boron, arsenic and aluminium was not observed in phosphorus implanted polysilicon with doses ranging between 10^{15} and 10^{16} ions/cm^2. In these cases, the sheet resistivity monotonously decreased with the increasing temperature to 750°C, above which all of the phosphorus atoms become electrically active. A similar tendency was observed in the annealing behaviour of the monocrystal silicon layers turned amorphous by ion implantation.

4. *Carrier concentration profiles*

In this part comparisons between the theoretical impurity concentration profiles and the carrier concentration profiles in single and polycrystalline silicon are shown. The theoretical depth profiles of the implanted atoms $n(x)$ are represented by the Edgeworth distribution

$$n(x) = \frac{D}{\sqrt{2\pi}\,\sigma_p} \exp\left(-\frac{x^2}{2}\right)\left[1+\frac{\sqrt{\beta}}{6}(x^3-3x)+\frac{5\beta}{72}(x^4-6x^2+3)\right.$$
$$\left.+\frac{\beta}{72}(x^6-15x^4+45x^2-15)\right]$$
$$x = \frac{x_p-R_p}{\sigma_p}, \quad \sqrt{\beta} = \frac{\mathrm{CM3}_p}{\sigma_p^3}, \tag{1}$$

where D means the dose implantation. The most probable projected range R_p, standard deviation σ_p, and third central moment $\mathrm{CM3}_p$ were calculated from Brice theory [7] by the method proposed by Mylroie and Gibbons [8] (hereafter refered to as BMG). The absolute values of the first and second central moments (R_p and σ_p) agree very well with those of Brice and Furokawa et al. [9] (usually well within 5% of the values given by Brice); and the third central moments are satisfactorily close to those of Winterbon [10, 11].

The 400 and 500°C annealing boron profiles bore no resemblance to the BMG profiles. The carriers concentration was very low in the region of theoretical R_p and grew to a maximum in the region of the damage peak concentration.

The 600°C annealing boron profiles and the BMG profiles were very similar in shape for doses ranging between 10^{14} and 5×10^{14} ions/cm^2, but the experimental carrier concentration remained very small compared to the doping concentration. The relative discrepancy between the experimental and calculated values of carrier concentration (η) increased with decreasing dose and for a fixed fluence, η determined from the profile annealed at 600°C was equal, within the experimental errors, to the η observed in the higher annealing temperature profile.

As the boron dose implantation was increased to about 10^{15} ions/cm^2, the carrier concentration approached that of the doping concentration after annealing above 600°C. The experimental profiles of carriers agreed closely with the BMG profiles in the surface region. It is clear from Fig. 4 that the implantation of boron into polycrystalline silicon films definitely exhibited more skewness in the profile than in single crystalline silicon. The discrepancy may be attributed to the thermal diffusion at such a low temperature as well as to the fact that in polycrystalline substrate the theoretical straggling expected from pure collision statistical considerations is too small [12].

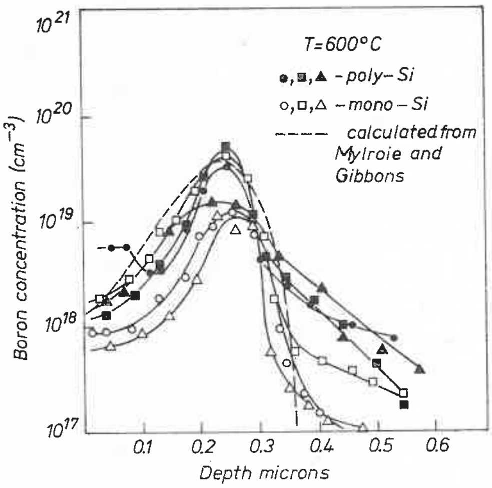

Fig. 4. Profiles of electrically active boron in polycrystalline Si films and single crystalline Si layers implanted for doses ranging between 8×10^{14} and 2×10^{15} ions/cm^2 after annealing at 600°C. Theoretical distribution is included for comparison

The profiles for boron dose implantations $D \approx 10^{15}$ ions/cm^2 annealed at temperatures above 700°C exhibit high electrical activity and broadening due to a very strong thermal diffusion. The discrepancy between the experimental and calculated profiles increases with annealing temperature. For polycrystalline films the apparent diffusion coefficients

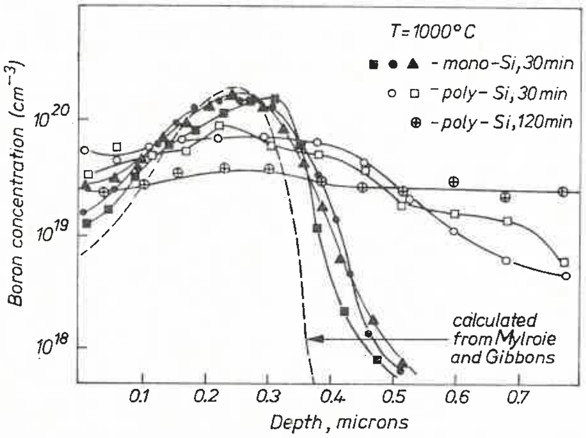

Fig. 5. Comparison between the profiles of 10^{15} B/cm^2 implanted at 60 keV after 30 and 120 min annealing at 1000°C

are always much bigger than for a single crystal. As can be seen from Fig. 5, in the polysilicon samples annealed at 1000°C for 30 min the carrier concentration was nearly uniformly distributed on the whole films.

The phosphorus profiles in polycrystalline films implanted with doses ranging between 10^{15} and 10^{16} ions/cm^2 and annealed at 600°C agree well with the BMG profile (usually well within 10% of the values given by Brice). The carrier profiles for implantations annealed at temperatures ranging between 700 and 1000°C exhibit broadening due to the thermal diffusion of phosphorus along the crystalline boundaries toward the surface and into the sample. The apparent diffusion coefficient increases with the increasing temperature.

Fig. 6 compares arsenic profiles measured in polycrystalline with the carrier distribution measured in single crystal silicon. The arsenic implantation was performed at 30, 45, 50 and 60 keV for a total dose ranging between 10^{13} and 10^{15} ions/cm^2. The samples were annealed at 600°C for 30 minutes in an argon atmosphere. It is clear from Fig. 6 that only for the single silicon samples the carrier concentrations are in agreement, within the experimental errors, to the theoretical profiles. A pronounced broadening in the depth distribution of arsenic atoms observed in the polycrystalline films suggests that thermal diffusion along the crystalline boundaries occurs even at such a low temperature. The range distributions show similar, nearly exponential tails, but they do not show a peak carrier concentration in the position predicted by the Brice theory for ions stopping in an amorphous substrate. The maximum of carrier density is near the surface, so that the profiles of the range distributions obtained in polycrystalline films are in agreement with the results reported for indium in single silicon samples [13].

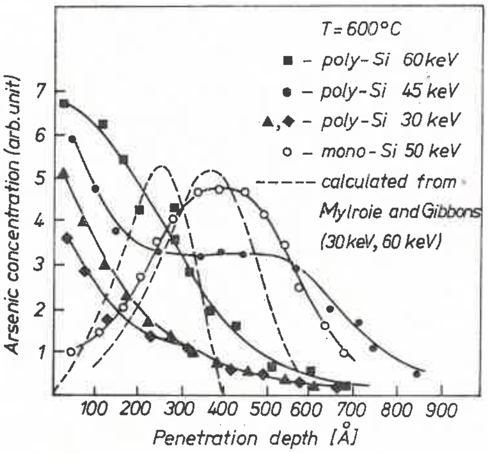

Fig. 6. Comparison between the profiles of electrically active arsenic implanted at 30, 45, 50, 60 keV after 30 min annealing at 600°C

For the indium and aluminium implanted films the carrier concentration remained very small compared to the doping concentration between room temperature and 1000°C for all doses of implantation, and the carrier profiles bore no resemblance to the BMG profiles.

5. *Discussion*

There are two schools of thought concerning the effects of the grain boundary upon the electrical properties of doped polycrystalline semiconductors [3]. Cowher and Sedwick [4] believe that the grain boundary acts as a sink for impurity atoms and consequently, the amount of impurity in the crystallite is reduced. This effect leads to a much smaller carrier concentration than the uniformly distributed impurity concentration. Kamins [14] believes that since the grain boundary usually consists of a few atomic layers of disordered atoms, there are a large number of trapping states. These trapping states reduce the number of free carriers and create a potential energy barrier which impedes the motion of carriers from one crystallite to another, thereby reducing their mobility.

Though the mechanism of carrier conduction and the change of polycrystalline silicon film properties with temperature are not yet perfectly understood, the annealing behaviours are explained as follows. For high dose implantation the sheet layers of polysilicon film were completly amorphous, therefore, in isochronal annealing the abrupt change of the sheet resistivity at about 450°C is interpreted as the change of the deposited amorphous layers into polysilicon. For low dose implantation, the impurity atoms become electrically active as the substrate temperature increases from 300°C up to 700°C. The effects of annealing of the lattice disorder produced during the implantation and changing the impurity atoms to carriers were not observed in indium implanted polysilicon film where the value of sheet resistivity is approximately constant between room temperature and 800°C.

In our investigations the ranges of implanted ions are always shorter than the film thickness, therefore, we can say that only the surface region influences the measured electrical properties at the low annealing temperature. The impurities begin to diffuse along the crystallite boundaries into the substrate at the temperature around 600°C. The decrease of the impurity atom concentration in the surface region induces the increase of the number of free trapping states and, therefore, the increase of the potential energy barrier which impedes the motion of carriers. So the diffusion causes the decrease of carrier mobility in polycrystalline silicon film and therefore causes the increase of the measured sheet resistivity. For low dose implantation, the effects of annealing of the lattice disorder, diffusion and changing the impurity atoms to carriers cause that the temperature at which electrical activity of implanted polysilicon films reached maximum is dependent on the implanted doses: with the increasing of a dose the temperature of the maximum activity falls.

The grain size of polycrystalline silicon is considered to increase with temperature around 850°C. The increase of the grain size causes the decrease of the total grain boundary area, and then the trapped impurity atoms at the grain boundary are emitted and redistributed to the crystal domain. These cause a further increase in carriers which in turn causes a further decrease of sheet resistivity. In boron implanted polycrystalline films the effect of an increase in carriers around 850°C is dependent on the implanted dose: with the increasing of a dose the relative difference between the maximum and minimum of sheet resistivity falls.

The boron, arsenic and phosphorus carrier profiles annealed after implantation up to 500°C bear no resemblence to the BMG distributions. Their peak concentration was closer to the damage peak and the experimental carrier concentrations remain very small compared to the doping concentration.

It was found that for doses of about 10^{15} ions/cm^2, the experimental boron and phosphorus distributions obtained in single and polycrystalline targets annealed at 600°C for 30 min can be described analytically with a considerable accuracy by the Edgeworth distribution. For all doses, heat treatment at temperature above 700°C produces the movement of impurity atoms along the crystallite boundaries toward the surface and into substrate. The apparent diffusion coefficients are dependent on the temperature and they are much bigger for polycrystalline silicon than for a single crystal.

It was found that in boron and phosphorus implanted polycrystalline films annealed at 1000°C for 120 min both the carrier concentration and the mobility were uniformly distributed in the film. The doping concentration was obtained by dividing the total implanted dose by the thickness of the polysilicon film. At a doping of 10^{18} B/cm^2 the hole concentration was only about 4×10^{17}/cm^2. As the implanted dose increased, the average carrier concentration increased and for a dose of 10^{15} ions/cm^2, the carrier concentration approached that of the doping concentration. The hole and electron mobility in all implanted polysilicon films are always much smaller than those in single crystalline silicon. The carrier mobility increases with the implantation dose. Our results for carrier concen-

TABLE I

The theoretical and experimental first (R_p), second (σ_p), and third ($CM3_p$) central moments for boron and phosphorus distributions into amorphous, single crystalline and polycrystalline silicon. The experimental moments were determined from profiles obtained in targets annealed at 600°C for 30 min

Ion	Energy [keV]	Central moment	Theoretical	Experimental	
			amorphous [microns]	mono-Si [microns]	poly-Si [microns]
Boron	70	R_p	0.2171	0.22	0.21
		σ_p	0.0592	0.06	0.065
		$CM3_p$	−0.0571	−0.04	−0.04
	50	R_p	0.1582	0.17	0.16
		σ_p	0.0491	0.05	0.05
		$CM3_p$	−0.0438	−0.02	−0.04
Phosphorus	70	R_p	0.0852	0.08	0.085
		σ_p	0.0333	0.04	0.03
		$CM3_p$	0.0201	0.03	0.01
	50	R_p	0.0608	0.07	0.062
		σ_p	0.0251	0.03	0.03
		$CM3_p$	0.0172	0.02	0.01

tration and mobility are quite similar to those calculated by Seto [3] for a boron implanted polycrystalline silicon film.

The computer program was extended to calculate three central moments of the experimental distribution. The comparison between the experimental and theoretical values of the average ranges, standard deviations and third central moments for boron and phosphorus implanted single crystal and polycrystalline substrates are given in Table I. It will be seen from the table that there is a considerable agreement between the experimental and theoretical values for R_p (usually well within 10%); differences in standard deviation do not go beyond 15%. For the third central moment the correspondence between the experimental and calculated values is found to be less good.

The larger experimental values of the standard deviation indicate that in practice there occur ranges shorter and longer than theoretically predicted. A small contribution to the found discrepancy, however, may have been caused by a difference between the tails of real doping distribution and Edgeworth distribution, at doping concentrations that are lower than could be measured with the existing apparatus.

The similarity of the distributions in single crystal and polycrystalline silicon, which is also reflected by the corresponding first and second central moments in Table I, proves that the polycrystalline silicon layers used in this study can be considered to be amorphous in respect to the boron and phosphorus stopping processes.

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