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S.S. Gill and B.J. Sealy

Royal Signals and Radar Establishment, St Andrews Road, Great Malvern, Worcestershire WR14 3PS, and Department of Electronic and Electrical Engineering, University of Surrey, Guildford, Surrey GU2 5XH, U.K.

ABSTRACT

A graphite strip heater and a multiply scanned electron beam have been used to anneal selenium implanted InP. The selenium dose ranged between 5 x 10^{12} and 1 x 10^{15} ions cm^{-2}, and the ion energy was 200 keV and all implants were performed into semi-insulating substrates at room temperature. The power density for the e-beam irradiations varied from 8 to 55 W cm^{-2} corresponding to temperatures up to 1100°C, a fixed temperature of 700°C was used for the graphite strip heater anneals. The majority of samples were coated with about 0.1 µm of pyrolytically deposited Si_3N_4 at 550°C, however some uncapped samples were also studied. Uncapped samples could not be electrically activated with the e-beam, but a capped low dose, 5 x 10^{12} cm^{-2}, implant gave an electrical activity of 17%. Activities of about 35% were obtained for doses of about 5 x 10^{14} cm^{-2} using either the graphite strip heater or the e-beam. These layers had peak electron concentrations in excess of 1 x 10^{19} cm^{-3}. We have also found that the Si_3N_4 deposition process at 550°C for 10 minutes can improve the structural properties of the implanted layer and render this surface layer conducting for a whole range of doses.

INTRODUCTION

Transient annealing is becoming a very popular method of recrystallising damaged layers and electrically activating implanted layers. The initial work indicated that annealing time as well as temperature is an important parameter. We have demonstrated this for ion implanted GaAs (1, 2) and InP (3) using a graphite strip heater. The use of multiply scanned electron beams (4, 5) and incoherent light sources (6) has also been demonstrated. In this paper, we compare the use of a graphite strip heater and a multiply scanned electron beam to anneal selenium implanted InP.

EXPERIMENTAL METHODS

Selenium ions were implanted in a non-channelling direction into <100> Fe-doped semi-insulating InP at room temperature. The ion doses were 5 x 10^{12} to 1 x 10^{15} cm^{-2} with an energy of 200 keV. A mixture of silane and ammonia was pyrolytically decomposed at 550°C for 10 minutes in order to encapsulate samples with about 0.1 µm of Si_3N_4. The graphite strip heater was used to carry out isothermal annealing at 700°C in the time range of 5 to 180 seconds in flowing nitrogen. The electron beam anneals were performed on 5 x 5 mm cleaved samples, in a vacuum of $\simeq 10^{-5}$ Torr, using an in-house commercial 1000 W electron beam machine (Lintech Instruments, UK). The power density of the 30 kV electron beam was set by changing the beam current in order to obtain values of 8 to 55 W cm^{-2} for exposure times of 0.5 to 4.5 seconds. The

unimplanted side of samples was coated with aquadag before being mounted on three silicon micro-points of 40 μm diameter and ≈ 400 μm in height to minimize heat loss through the back surface via thermal conduction (5). After annealing both the Si_3N_4 and aquadag was removed by dissolution in concentrated hydrofluoric acid and washed in deionised water. Ohmic contacts were formed by alloying tin dots at 300°C for one minute on the four corners of chemically etched clover-leaf samples. Sheet Hall effect measurements were performed using the Van der Pauw technique to obtain carrier concentration, Hall mobility, and resistivity. Differential Hall measurements were used to obtain carrier concentration profiles of the implanted ions. The etchant used was a solution of 5% by weight of iodic acid in H_2O, which gave an etch rate of 400 Å/minute. Rutherford backscattering using 1.5 MeV helium ions, both in aligned and non-aligned directions, was used to obtain structural information.

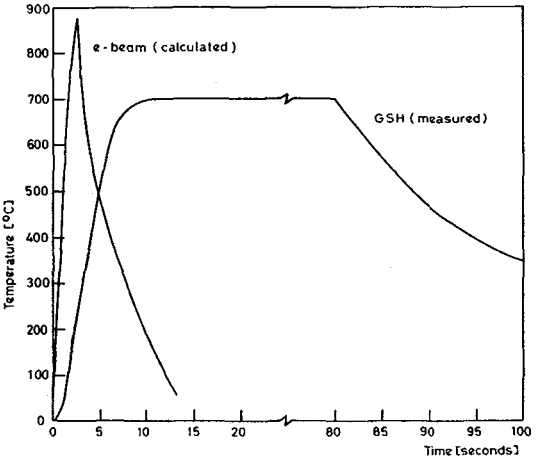

FIG.1. TEMPERATURE / TIME PROFILES

RESULTS

Figure 1 shows the temperature-time excursions of samples for two typical annealing conditions using the electron beam and the graphite strip heater.

Multiply scanned electron beam annealing

Initially we studied uncapped low dose implants irradiated for 1 second at a variety of power densities since it was hoped that decomposition would not occur in this short time. Rutherford backscattering (RBS) spectra showed that recrystallisation had taken place with the lowest χ_{min} values of ≈ 5% occurring in the range 24 to 34 W cm^{-2} (Table 1). This χ_{min} value corresponds to that of good crystalline InP. However, there is still a significant amount of damage within the implanted layer detectable by RBS (5). None of these samples were electrically active. We concluded that higher power densities or longer times are necessary to activate the implanted ions. This implies that the surface should be protected during irradiation, since there were obvious signs of decomposition at power densities above about 40 W cm^{-2} (Table 1).

Figure 2 illustrates how the sheet electrical properties of capped samples, implanted with a dose of 5 x 10^{12} cm^{-2} vary with irradiation time for a power density of 55 W cm^{-2}. The highest electrical activity of 17% occurred following an irradiation of 2 seconds duration. The Si_3N_4 visibly fails for times above 2 seconds at this power density.

Capped samples implanted with a dose of 3.6 x 10^{14} cm^{-2} were also studied as a function of power density for a fixed irradiation time of 2.5 seconds (figure 3). The results show that saturation values of electrical properties occur in the range 25 to 33 W cm^{-2}. For exposures in excess of 33 W cm^{-2}, the Si_3N_4 cap shows signs of failure.

POWER DENSITY (W/cm2)	x_{min} (%) 5 x 10^{12} Se+/cm^2	1.10^{13} Se+/cm^2
As implanted	23.0	46.0
15	12.9	19.1
18	9.2	12.8
21	6.5	9.3
24	4.9	6.3
30	5.3	6.5
40	5.9	6.9
45	6.5	8.7

TABLE 1 Rutherford backscattering results for low dose implants, annealed without an encapsulant, for various e-beam power densities. The exposure time was 1 s, the ion energy 200 keV, and the implants were performed at room temperature

Thermal pulse annealing with the graphite strip heater (GSH)

A temperature of 700°C was chosen to study the electrical properties as a function of time following isothermal annealing using the GSH, the results being shown in figures 4a, 4b and 4c. The zero time data points correspond to the electrical properties of samples which have been heat treated at 550°C for 10 minutes during the Si_3N_4 deposition process. The sheet Hall mobility increased with annealing time for all the doses studied (figure 4a) which suggests that the lattice recovers its crystallinity on annealing. However the electrical activity behaves differently from the mobility (figure 4b). The resistivity is a combination of these two parameters (see figure 4c). For doses up to 1 x 10^{14} cm^{-2} the activity increases with increasing time however for higher doses (5 x 10^{14} and 1 x 10^{15} cm^{-2}) the activity decreases with increasing time. Saturation values of electrical properties are attained after a time of about 40 seconds.

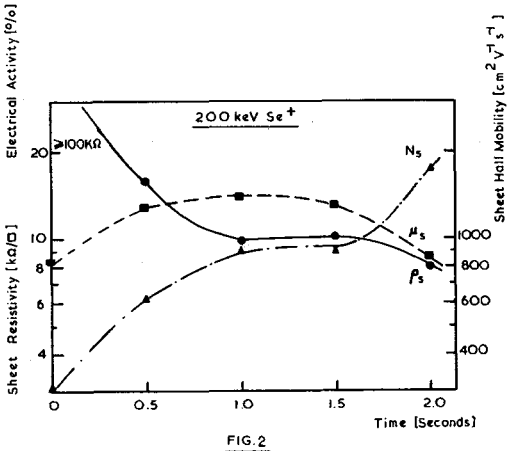

FIG.2

(▲) Electrical activity, N_s, (■) Sheet Hall mobility, μ_s, and (●) Sheet resistivity ρ_s, as function of exposure time for 5 x 10^{12} Se^+ cm^{-2}, 200keV room temperature implants into InP E-beam power density was 55 W cm^{-2}, all samples capped with CVD-Si_3N_4.

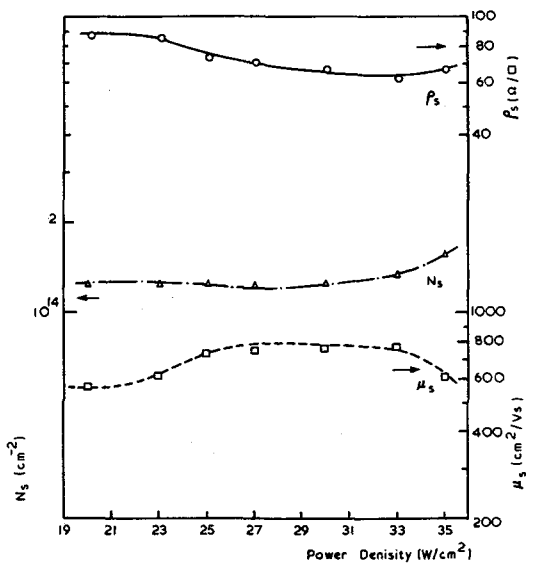

FIG. 3

(Δ) sheet electron concentration (N_s), (□) sheet Hall mobility (μs) and, (○) sheet resistivity (ρ_s) as a function of e-beam power density, for a dose of 3.6 × 10^{14} Se^+ cm^{-2}, 200keV room temperature implants into InP. All exposures were for 2.5 seconds.

The fact that samples are electrically active following the Si_3N_4 deposition process implies that significant recrystallisation has occurred during this treatment. This was investigated using Rutherford backscattering (Table 2). Doses of 1 x 10^{14} and above produced a backscattered yield near the surface, for an aligned spectrum which equalled the yield from a non-aligned sample, indicating that the surface had become amorphous (7). This amorphous layer was about 0.2 μm thick (7). A dose of 1 x 10^{13} cm^{-2} produced significant damage but the surface did not become amorphous. The Si_3N_4 deposition process modified all the aligned spectra (Table 2). Thus the heat treatment of samples during the Si_3N_4 deposition process produces significant

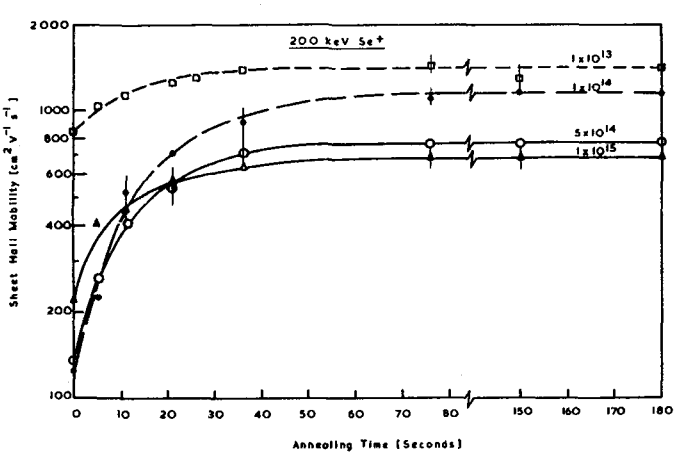

FIG. 4a

Sheet Hall mobility as function of annealing at 700°C using the graphite strip for (□) 1 × 10^{13} ; (●) 1 × 10^{14} ; (○) 5 × 10^{14} and (Δ) 1 × 10^{15} Se^+ cm^{-2}, 200 keV implants into InP at room temperature.

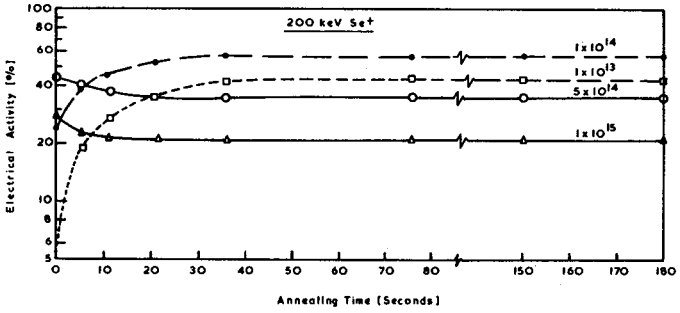

FIG. 4b

Electrical activity as function of annealing time. Details as in figure 1a.

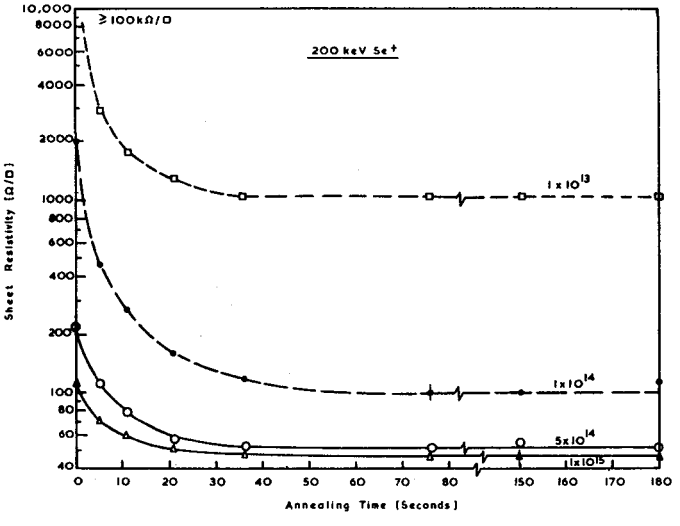

FIG. 4c

Dose [Se+ cm^{-2}] \ x_{min} [%]	Ion Implanted	Ion Implanted + Si_3N_4 Deposition
1 x 10^{13}	46	9
1 x 10^{14}	68	18
5 x 10^{14}	75	44
1 x 10^{15}	82	72

TABLE 2 Recovery of crystallinity of ion implanted InP (indicated by damage parameter x_{min}), after the Si_3N_4 deposition process at 550°C for 10 minutes

recrystallisation of the damaged layers caused by ion implantation. An example of electron concentration profile for a sample irradiated with an e-beam power density of 30 W cm^{-2} for 2.5 seconds is shown in figure 5. Also shown is a profile obtained from a similar sample annealed with the GSH at 700°C for 80 seconds.

DISCUSSION

The deposition of the Si_3N_4 encapsulant at 550°C produces significant recrystallisation and all samples become conducting (figure 4). We suggest that this conductivity has two components due to (a) the implanted dopant and (b) the residual damage (Table 2). For doses of 1 x 10^{14} cm^{-2} and below, the electrical activities increase with increasing annealing time using the GSH (figure 4b). This is to be expected since the damage is being progressively removed with annealing time. The fact that the mobility increases with time is also indicative of the removal

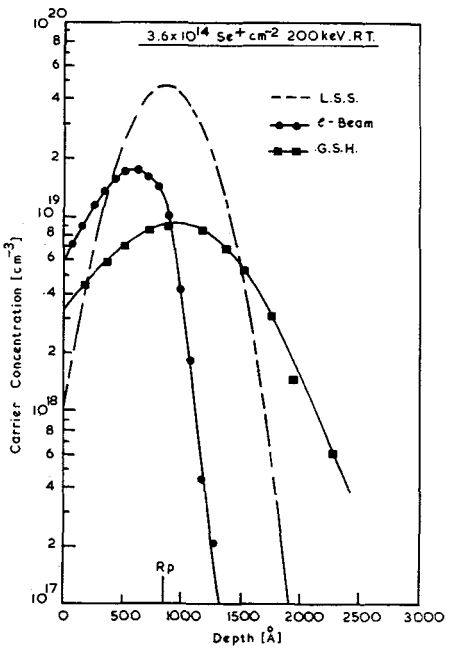

FIG. 5

Carrier concentration depth profiles for selenium implanted InP and annealed using a graphite strip (700°C for 80 seconds) and e-beam (30 Watts cm^{-2} for 2.5 sec). Also the corresponding LSS profile is presented for comparison.

of damage. However, for doses of 5 x 10^{14} cm^{-2} and above the electrical activity decreases with annealing time. We suggest that the activity at zero time is mainly due to residual damage (figure 4b). As the annealing time increases the net activity reduces due to a reduction in the contribution from the damage. Thus we conclude that the saturation values of activity (figure 4b) include a contribution both from damage and the implanted ions, the relative amounts depending on the dose. These conclusions apply both to GSH and e-beam anneals.

It is interesting to consider the estimated temperature reached by the samples annealed with the e-beam. In figure 2, the overall activity increases with irradiation time. However, times of 1.0 and 1.5 seconds produce similar electrical results which is strange because the peak temperature reached by the samples increases from about 800°C to 1000°C in this time interval. The failure of the Si_3N_4 cap following 2 second irradiation at 55 W cm^{-2} is understandable because the peak temperature reached is about 1100°C. Thus it is possible to anneal up to 1000°C provided that the irradiation time is short and that the sample is adequately encapsulated.

From figure 3, it was noted that saturation values of electrical properties occurred for e-beam power densities between 25 and 33 W cm^{-2} for a 2.5 second exposure. In this power density range, the peak temperature reached by the sample increases from about 750°C to about 900°C. The Si_3N_4 cap begins to fail at 35 W cm^{-2} which corresponds to a maximum temperature of about 940°C. The plateau regions in figures 2 and 3 exist even though the annealing temperature increases by about 200°C in this region. We suggest that this is due to the annealing out of the damage contribution to electrical activity and the simultaneous improvement in electrical activity from the implanted ions.

From figure 5, it was noted that the selenium profile is shallower for the e-beam compared with the predicted LSS profile. This may be due to damage induced diffusion towards the surface, caused by ion implantation, e-beam irradiation and the Si_3N_4 encapsulant deposition. The low activation efficiency also indicates presence of damage even after the anneal treatment, this was further confirmed by the high value of X_{min} from RBS measurements.

CONCLUSIONS

A GSH and a multiply scanned electron beam have both been used successfully to activate a wide range of room temperature selenium implants in InP. The results of the isothermal and isochronal annealing experiments indicate that damage plays an important contribution to the electrical properties of the implanted InP. This is the first detailed study of the annealing kinetics of selenium implanted InP which clearly demonstrates the contribution of damage to electrical activity. In addition; we have demonstrated the feasibility of very high temperature ($\sim 1000^{o}C$) short time anneals for capped InP.

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References

(1) R. K. Surridge, B. J. Sealy, A. D. E. D'Cruz and K. G. Stephens, Inst. of Phys. Conf. Ser. No. 33a (Bristol 1877) 161.

(2) B. J. Sealy, R. K. Surridge, S. S. Kular and K. G. Stephens, Inst. of Phys. Conf. Ser. No 46 (Bristol 1979) 476.

(3) S. S. Gill, B. J. Sealy, P. J. Topham, N. J. Barrett and K. G. Stephens, Elec. Lett. 17 (1981) 623.

(4) N. J. Shah, H. Ahmed, I. R. Sanders and J. F. Singleton, Elec. Lett. 16 (1980) 433.

(5) Sukhdev. S. Gill, Appl. Phys. Lett. 4 (1982) 729.

(6) D. E. Davies, P. J. McNally, J. P. Lorenzo and M. Julian, IEEE Electron Device. Lett. EDL-3 (1982) 102.

(7) S. S. Gill, B. J. Sealy and K. G. Stephens, J. Phys. D. Appl. Phys. 14 (1981) 1915.