Proximate capless annealing of GaAs using a controlled-excess As vapor pressure source

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A new, capless annealing technique for GaAs, which utilizes a controlled-excess arsenic vapor pressure has been studied. The excess arsenic vapor is provided by the thermal decomposition of InAs and is about 100 times larger than the arsenic pressure of thermally decomposing GaAs for temperatures of 800–900 °C. This excess pressure forces Si implants to activate predominantly on donor sites for doses of $(2–50) \times 10^{12}$ cm^{-2} studied thus far. A SiF + dose of 5×10^{12} cm^{-2} and implant energy of 250 keV annealed at 900 °C for 30 min produced a sheet electron concentration of 3.5×10^{12} cm^{-2} and mobility of 4400 cm^2 V^{-1} sec^{-1}. Photoluminescence studies show that the annealed surfaces must be proximate during anneal to avoid buildup of impurities at the surface. A model based on GaAs evaporation and buildup of bulk impurities on the surface is proposed to explain the results.

The direct ion implantation of wafers of bulk semi-insulating GaAs is a promising technology for microwave and high-speed logic devices.[1,2] The key issues for this technology are (i) the ability to reproducibly grow bulk semi-insulating GaAs crystals with a chromium or controlled compensating dopant concentration of $\leqslant 10^{16}$ cm^{-3}, which are stable during device processing, and (ii) the ability to implant and activate dopants to produce carrier profiles which vary less than 5% across the wafer and from run to run.

In the past, Cr-doped semi-insulating GaAs has been widely used for device research. However, many workers have found this material to be unstable during hot processing and have observed such effects as excessive surface and bulk conductivity after annealing,[3] out diffusion of Cr during annealing,[4] and nonreproducible implant activation. Recently, improved GaAs crystals have been grown by the liquid-encapsulation method[5] without intentional doping and by the horizonal Bridgman method using controlled pressures of Ga$_2$O during growth.[6]

Several successful implantation techniques have been reported and are classified as either "cap"[7–9] or "capless".[10–12] Most cap techniques use layers of Si$_3$N$_4$ and/or SiO$_2$ on the GaAs surface to protect against thermal decomposition during anneal. The capless techniques retard decomposition by supplying a source of arsenic such as crushed GaAs,[10] AsH$_3$,[11] or by proximate GaAs wafers during anneal. Both of those methods, cap and capless, reported so far suffer from various drawbacks such as excess stress due to capping layers, difficulties in controlling impurity activation, etc.

In this letter we report on a new capless anneal technique for ion-implanted GaAs, which utilizes the thermal decompostion of InAs to establish a controlled and known excess As atmosphere during annealing. The excess As is due to the fact that the As pressure in equilibrium with thermally dissociated InAs is about 100 times larger than that for GaAs for annealing temperatures of 800–900 °C as shown in

Fig. 1.[13] The InAs ambient coupled with GaAs proximate wafers provides a reliable and reproducible method for (i) preventing decomposition and evaporation of GaAs surface, (ii) annealing radiation damage, and (iii) controlling the activation of implanted dopants including the amphoteric impurities Si and Ge. We have also studied the phtoluminescent properties of annealed samples and propose a new model for the surface accumlation of acceptor impurities reported by previous workers.[14,15]

Two different types of GaAs bulk wafers were used in this study. Cr-doped semi-insulateing material from Sumitomo Electric Co. with estimated Cr concentrations of $(5–10) \times 10^{16}$ cm^{-3}, and semi-insulating GaAs crystals grown by the horizontal Bridgman method using fused quartz vessels and a controlled Ga$_2$O vapor pressure during growth. Both types were used for the implant anneal studies, while only the oxygen-grown material was used for the anneal and
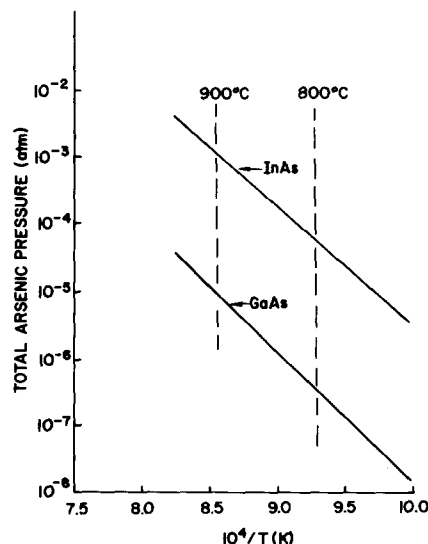

FIG. 1. Arsenic vapor pressure vs 10^4/T K^{-1}, for the dissociation of GaAs and InAs.

photoluminescence studied. The wafers for the implant studies were (100) oriented and chemically polished. They were final etched in 50:3:1, $H_2O:H_2PO_4H_2O_2$ to remove about 0.2 μ and spun dry.

The implantations were performed using SiF + ions at doses and energies ringing from $(5-50) \times 10^{12}$ cm^{-2} and 250–400 ev, respectively. The anneal experiments were performed using the apparatus shown in Fig. 2. Several features of the apparatus should be notes. First, it should have a small confinement volume to minimize loss of As from the decomposition of the InAs. This can be accomplished using the fixture in Fig. 2, with a small hole through which the chamber can be vacuum baked at 200–400 °C to drive off water and oxygen and then back filled with hydrogen. The small hole then retards the loss of As during anneal. Preferably, the confinement volume could be "open" during bake and "closed" during anneal. This can be achieved using a quartz "bell jar" fixture, which can be lowered over the GaAs sam-
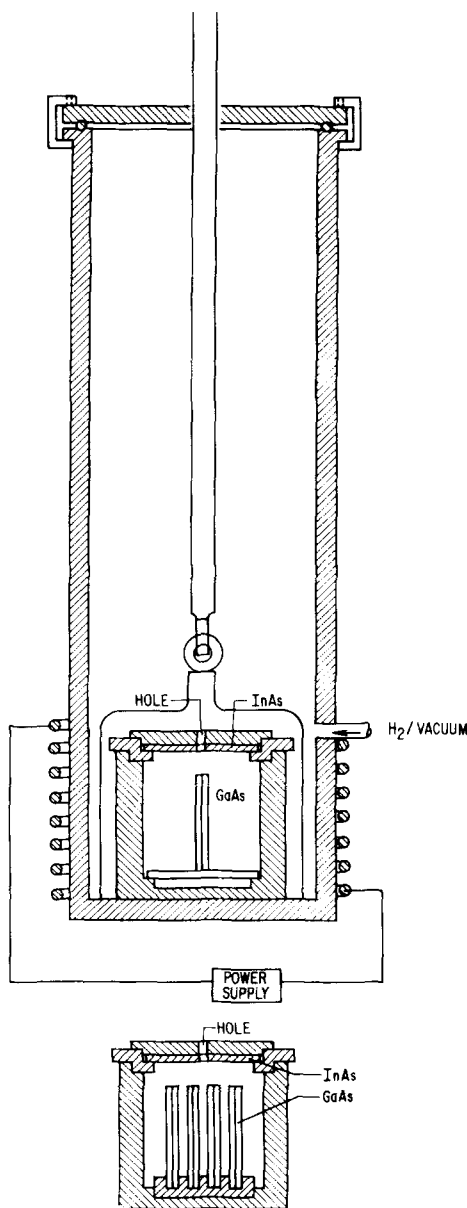

FIG. 2. Apparatus for annealing in the presence of InAs.

ples and InAs after the bake. Secondly, as will be discussed later, it is important that an implanted GaAs surface be proximate to another polished or implanted GaAs surface during anneal. It has been found that the presence of InAs during anneal is a necessary but not sufficient condition for controlled activation and that proximate contrac of implanted surface is also necessary.

The anneals reported here were done at 850–900 °C for 30 min in a hydrogen ambient.

It is also important to note the role of the In As during anneal especially for the group IV dopants Si and Ge. If the prevention of decomposition of the implanted surfaces were the main issue, then proximate contact wuld be sufficient. However, a higher arsenic pressure than that provided by the decomposition of GaAs is necessary to cause the activation of Si implants to occur predominately as an n-type dopant. It is known, for example, that the liquid phase epitaxial growth of Si-doped GaAs at 900 °C leads to a highly compensated material.[16] The arsenic pressures for liquid phase epitaxy and proximate contact anneal are nearly the same, and thus the proximate contace method could leak to activation of compensated material. A method similar to the proximate method has yielded results for Si implants, which suggest compensation is occuring.[17] The higher As pressure from InAs is expected to drive the Si on donor sites according to the reaction[18]

$$N_D/N_A = K\,[P_{As_4}]^{1/2},$$

where N_D is the concentration of Si on donor or gallium sites, N_A is the concentration of Si on acceptor or arsenic sites, K is a thermodynamic constant, and PP_{As_4} = pressure of As$_4$. This equation is arbitrarily shown for As$_4$ and could be written with different constants for the As$_2$ species. We have obtained the following results for this method. For SiF$^+$ implants of 5×10^{13} cm^{-2} at 400 keV and annealed at 850 °C for 30 min the sheet electron concentration was 2.5×10^{13} cm^{-2} V^{-1} sec^{-1}. For the same dose and for an anneal at 900 °C for 30 min the sheet electron concentration was 2.7×10^{13} cm^{-2} and the mobility was 2530 cm^2 V^{-1} sec^{-1}. For doses of $(5-10) \times 10^{12}$ and anneal at 900 °C for 30 min the n-type activation was about 50%, and the mobilities were greater than 4000 cm^2 V^{-1} sec^{-1}.[19] Table I demonstrates the uniformity of results of SiF$^+$ implant dose of 5×10^{12} cm^{-2} at 250 keV for six different wafers annealed simultaneously at 900 °C for 30 min. Note the mobility value of greater than 4000 cm^2 V^{-1} sec^{-1}.

In order to further characterize this annealing technique, photoluminescence studies were made on annealed nonimplanted high-purity oxygen-grown semi-insulting material.[6] The results for a 900 °C 30-min anneal are shown in Fig. 3. Curve 1 depicts the data obtained from a wafer of the

TABLE I. Uniformity of electrical parameters of wafers annealed simultaneously at 900 °C for 30 min.

$\rho_s(\Omega/\square)$	412	415	403	356	395	408
N_s $_{eff}$(cm^{-2})$\times 10^{-12}$	3.54	3.64	3.5	4.2	3.7	3.55
μ_{eff}(cm^2/V sec)	4278	4130	4409	4118	4276	4304

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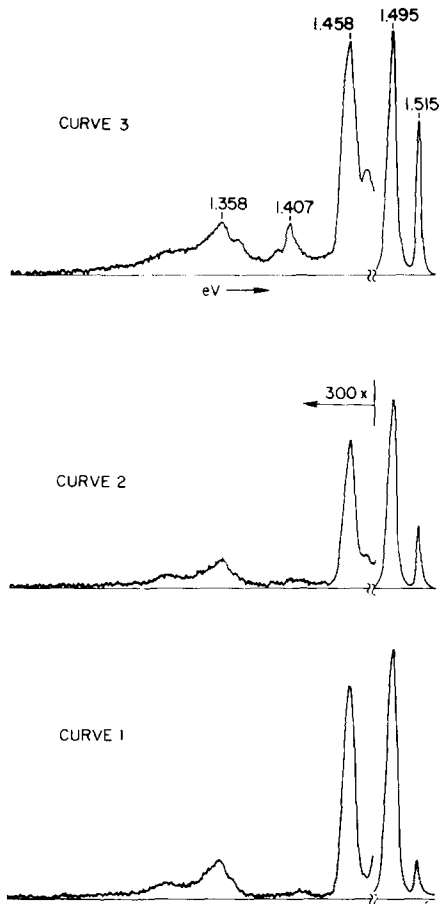
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FIG. 3. 4 K photoluminescence spectra of annealed high-purity oxygen grown GaAs: Curve 1, starting material, a bulk crystal annealed at 750 °C for 48 h; Curve 2, proximate surfaces of starting materials annealed with InAs at 880 °C for 30 min; Curve 3, *nonproximate* surface *with or without* InAs or *proximate* surfaces *without* InAs anneal at 880 °C, 30 min.

"starting" crystal, which has received a 750 °C anneal for 48 h to lower the concentration of some as yet unidentified heat treatable acceptor impurity or defect.[20] Note the presence of the carbon (1.495 eV) peak, a trace of the Mn (1.407 eV) peak, and some copper (1.358 eV). From previous work we estimate the carbon concentration to be $\approx 10^{15}$ cm^{-3} and the Cu and Mn to be $\leqslant 10^{14}$ cm^3. We surmise that the reason the oxygen-grown GaAs is semi-insulating is due to the presence of a deep donor level related to the presence of Ga_2O vapor during growth at a concentration of $(1-2) \times 10^{16}$. This deep donor partially compensates some of the shallow acceptor levels, which to a large extent can be attributed to carbon, which is present at a concentration of about 10^{15} cm^{-3}. These shallow acceptor levels in turn tend to overcompensate residual shallow donors (mainly silicon donors) at a concentration of less than 10^{15} cm^{-3}.

Curve 2 represents the photoluminescence response of wafer surfaces, which were annealed in proximate surface contact with other in the presence of InAs. The results clearly indicate that this anneal procedure does not produce any noticeable change in the photoluminescent properties of the surface. Furthermore, electrical measurements confirm that the resistivity of the surface remains unchangerd.

If on the other hand the GaAs wafers were heat treated under the conditions as follows: (i) surfaces in proximate

contact without InAs, or (b) surfaces not in proximate contace with and without InAs, Curve 3 resulted. Under those conditions, a distinct increase in the Cu and Mn signals is being observed. In addition, the surfaces of these samples are low-resistivity *p* type. This effect has been observed by other works and has been ascribed to outdiffusion of Mn (Ref. 14) during anneal and to vacancies.[15] The conditions for Curve 3 are such that they lead to larger free evaporation of GaAs during anneal than the conditions for Curve 2. Therefore we suspected that the enhancement of the Mn peak in Curve 3 was a result of the evaporation of GaAs, which leaves behind an accumulation of Mn and other impurities on or near the surface. This hypothesis was tested by annealing a wafer which was half covered by a 2-μ-thick layer of $Ga_{0.4}Al_{0.6}As$ grown by molecular beam epitaxy. Before the anneal, the photoluminescence was nearly the same as Curve 1 for both the covered and uncovered portions of the wafer. After a 900 °C, 30-min, nonproximate-contact anneal in H_2 with InAs present, the uncovered portion of the wafer showed a photoluminscence spectra similar to Curve 3; whereas the GaAl-As-covered portion was similar to Curve 2. Furthermore, selectively etching-away the GaAlAs layer after annealing revealed that 0.1 μ of GaAs had evaporated from the uncovered portion of the wafer during the anneal.

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[1] B. M. Welch, F. H. Eisen, and J. A. Higgins, J. Appl. Phys. **45**, 3685 (1974).
[2] Proceeding of the AVS Symposium on High-Speed, High-Frequency Integrated Circuits, edited by L. F. Eastman, 1980. (unpublished).
[3] J. P. Donnelly, C. D. Bozler, and W. T. Lendley, Solid-State Electron. **20**, 273 (1977).
[4] A. M. Haber, G. Morillot, and N. T. Link, Appl. Phys. Lett. **34**, 858 (1979).
[5] H. M. Hobgood, G. W. Eldridge, D. L. Barrett, and R. N. Thomas, *IEEE III-V Process Technnology Wrokshop, Santa Cruz, California*, 1980. (IEEE, New York, 1980).
[6] R. J. Chicotka, H. S. Rupprecht, and J. M. Woodall, in Ref. 5.
[7] B. Molnar, J. Electrochem. Soc. **123**, 767 (1976).
[8] J. Gyulai, J. W. Mayer, I. V. Mitchell, and V. Rodriguez, Appl. Phys. Lett. **17**, 332 (1972).
[9] J. P. Donnelly, W. T. Lindley, and C. E. Hurwitz, Appl. Phys. Lett. **27**, 41 (1975).
[10] A. A. Immorlica and F. H. Eisen, Appl. Phys. Lett. **29**, 94 (1976).
[11] J. Kasahara, M. Arai, and N. Watanabe, J. Appl. Phys. **50**, 541 (1979).
[12] B. Molnar, Appl. Phys. Lett. **36**, 927 (1980).
[13] C. Pupp, J. J. Murray, and R. F. Pottie, J. Chem Thermodyn. **6**, 123 (1974).
[14] P. B. Klein, P. E. R. Nordquist, and P. G. Siebermann, J. Appl. Phys. **51**, 4861 (1980).
[15] W. Y. Lum and H. H. Wieder, J. Appl. Phys. **49**, 6187 (1978).
[16] H. Rupprecht, J. M. Woodall, W. C. Konnerth, and N. G. Pettit, Appl. Phys. Lett. **9**, 221 (1966).
[17] C. Anderson, K. V. Vaidyananathan, H. L. Dunlap, and G. S. Kamath, J. Electrochem Soc. **127**, 925 (1980).
[18] J. M. Whelan, J. D. Struthers, and J. A. Dizenberger, Met. Soc. Conf. **5**, 141 (1959).
[19] Recently, we have moved this activation to 90–100% using better cleaning procedure on the backside of the implanted wafers.
[20] J. M. Woodall and J. F. Woods, Solid State Commun **4**, 33 (1966).

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