

Ion implantation and laser treatment of III–V compound semiconductor: A brief report

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Abstract. The progress in the area of applications of ion implantation and laser treatment to III-V semiconductors is reviewed. The achievements till today are discussed along with the yet unresolved problems.

Keywords. Ion implantation; laser treatment; compound semiconductors.

1. Introduction

GaAs and other III–V compound semiconductors have been identified as “materials for the future”, especially in the context of strategic applications in the areas of advanced electronics and optoelectronics, in view of some of their unique and interesting properties which cannot be realised in elemental semiconductors such as Si or Ge (Pearton *et al* 1987). In GaAs, for instance, the electron effective mass m_e^* is only 7% of its value in silicon and hence the intrinsic operating speeds of devices based on GaAs are significantly higher. This fact is accentuated by the possibility of realizing semi-insulating substrates which lower parasitic capacitances and eliminate the need for complicated isolation structures common in silicon technology. Also, GaAs has a direct bandgap of 1.4 eV which is wider than the indirect bandgap of 1.1 eV of silicon, making it a very useful material for optoelectronic and elevated-temperature applications. Further, GaAs and some other III–V compound semiconductors have exceptionally high values of radiation hardness as compared to Si. This is an important property in specific applications in aerospace, defence and nuclear electronics. Another interesting and useful feature of III–V compound semiconductors is the possibility and relative ease of alloying them with a view to tailoring their physical properties, such as lattice parameter (for realizing epitaxy criteria), band gap etc (Palmstrom and Morgan 1985). In spite of these possibilities and their remarkable features, III–V compound semiconductor-based electronics is not common at this point of time in view of certain difficulties faced in converting the corresponding science into technology. It has not yet been possible to fabricate high performance bipolar transistors based on GaAs because of the low minority carrier lifetime in this material. Also GaAs has a lower thermal conductivity as compared to silicon and hence there are intrinsic power handling difficulties. Even during processing, if the temperature is raised to a value required for carrier activation of implants the surface tends to dissociate leading to out-diffusion of specific atoms (as in the case of GaAs) and generation of a multiplicity of undesirable effects. Further, GaAs does not support a stable surface oxide with low interface state density which makes it difficult to realize electronically tenable MOS structures in this material. In addition to these hurdles which stem from the basic materials features of III–V semiconductors there are other difficulties as well which relate to adoptability of these materials to advanced processing technologies

which are central to the concept of miniaturization and are at the heart of modern microelectronics. It is clear that III-V compound semiconductor electronics cannot make the projected impact unless miniature configurations can be built into these systems stably and reproducibly by successful applications of advanced doping schemes. It is equally important to establish methods and procedures for realizing true electronic contacts to these materials so that an operational circuit integration is achieved in this material.

2. Methods

Foremost amongst the advance doping schemes in microelectronics are the techniques based on ion implantation (Mayer *et al* 1970; Crowder 1973) and laser treatment of surfaces (Honnhout 1981; Poate and Mayer 1982). In the ion implantation method of surface modification selected ionic species having an energy of a few tens to a few hundred kilo electron volts are bombarded on material surfaces in a clean environment under vacuum (pressure $< 10^{-6}$ Torr). By controlling the ion energy, target temperature during implantation, and the orientation of crystal planes with reference to the direction of incidence of the ion beam, one can control the dopant profile below the surface to a considerable degree of accuracy. Also by focussing the beam down to micron-order dimensions a direct writing of doping features can also be achieved. However, implantation being a directed energy processing technique, it has an associated hazard in terms of creation of damage and disorder in the implanted layers. Unless a suitable post-treatment either in the form of thermal or laser anneal is imparted to the sample the dopants cannot be activated and the desired effects cannot be achieved. This post-treatment has been successfully realized in the case of Si but not yet in the case of III-V compound semiconductors. Even if a way can be found out to achieve a suitable post-treatment there is yet another problem in the case of compound semiconductors which is absent in elemental semiconductors such as silicon. This problem relates to the availability of two or more chemically as well as electronically non-equivalent sites in compound semiconductors and the relative preference shown by dopants towards them in so far as post-treatment occupancy is concerned (Pearton *et al* 1987). If one implants a group IV species such as silicon in a III-V compound such as GaAs one would get *n*-type material if Si preferentially occupies Ga sites, while one may get a *p*-type material if it primarily occupies As sites. But if the preference shown by a given dopant is not significantly asymmetric then major compensation effects can occur and significant dopants are wasted in so far as their usage in electronic action is concerned. This indeed is the case with many dopants which are amphoteric in character. Different suggestions have been made and partly experimented with in this context such as, for instance, dual implantation (Choudhari and Armiento 1987; Hyuga *et al* 1987). However, the issue is still wide open since none of these attempts have been truly successful in enhancing the dopant activity beyond a few tens in terms of percentage (and that too in a limited number of cases) (Pearton *et al* 1987), in contrast to the case of silicon wherein a near hundred per cent activation of dopants has been demonstrated and routinely achieved. Apart from the dopant related mutual compensation effects there are intrinsic defect-related compensation effects whose existence has been identified but the precise nature of effects is not yet understood

(Pearson *et al* 1987). It is generally agreed that the so-called EL2 level related to the As antisite complex is the main point defect in GaAs, however the exact local structure of this and other such compensating defects and their implications for definition of local electronics states are yet to be understood. There is a lack of significant thermodynamic and kinetic data on solubility, diffusivity and activation kinetics of implants and the relationship of these variables to electrical activation. In addition to the question of electrical activation there is another important aspect pertaining to the role of dopants in GaAs which deserves attention. This relates to impurity-induced passivation of stresses in grain boundary regions in this material, which has a bearing on realization of routine production of GaAs-based integrated circuits (Hyuga *et al* 1985). It has been demonstrated that unless suitable pre-doping or pre-conditioning is effected in GaAs it is extremely difficult to achieve a degree of lateral uniformity which is essential for large scale integration and areal multiplication.

As stated earlier there is another major technological problem in the context of III-V compound semiconductors which has to be solved before any true impact of such technology can be effected; and this relates to achieving good quality ohmic contacts to these materials; especially their *n*-type doped versions. The use of alloying contacts based on eutectics such as AuGeNi is not satisfactory for several reasons including limits on downscaling, irreproducibility and unreliability. Hence it is desirable to work on the possibilities of non-alloying ohmic contacts such as, for instance, by making very highly doped *n*-regions (10^{20} cm^{-3}) or by suitably controlling solid phase reactions of metals with GaAs. The ion beam-based method of controlled interface reaction, *viz.* ion-beam mixing (Tsauro *et al* 1979; Mayer and Laqu 1981; Godbole *et al* 1985; Ogale *et al* 1985) is being looked at as a promising solution in this regard, though a lot remains to be done in this context.

Ion-beam mixing (Tsauro *et al* 1979; Mayer and Laqu 1981) is a simple variant of the basic implantation method wherein a composite sample comprising a substrate and an overlayer or a multilayer structure is bombarded with high energy ions (100–400 KeV) so as to induce atomic mixing in the layers. In this method the high kinetic energy of ions is used to impart transient motions to the atoms leading to non-equilibrium mixing effects; the primary ion-atom energy transfer process being governed by the so-called nuclear energy loss cross-section. This technique allows low temperature alloying effects over controlled depth scale (defined by the ion energy) and the stoichiometry of the mixed layers can also be controlled by controlling the relative thicknesses of the deposited layers. In so far as alloying is concerned the ion-beam mixing technique is superior to the method of direct ion implantation, because in the latter case a very high dose of implantant ($> 5 \times 10^{17} \text{ ions/cm}^2$) is essential to realize the formation of concentrated alloys and this is intrinsically associated with severe sputtering effects leading to erosion of the surface layers. Ion-beam mixing has been demonstrated to be a useful and technologically viable process in the case of silicide formation for making contacts to silicon-based devices; however its applicability in the case of III-V semiconductor based devices remains to be examined.

In addition to its use for the controlled doping process and for alloying of overlayers via ion mixing scheme, the technique of ion implantation also holds considerable promise in the context of barrier layer synthesis in the form of stable surface oxides and nitrides. As an example a recent study from AT and T Bell

laboratories may be quoted (Pearson *et al* 1988) wherein oxygen implantation was used to achieve chemically induced compensation in AlGaAs which was found to be stable up to a temperature of 950–1000°C. Also, another area which needs considerable work is implantation through the barrier layer at elevated temperature to induce in-process damage recovery; with an eye on the nature of interface mixing effects between the insulating overlayer and the underlying semiconducting material.

Finally, in elaborating on the role of ion implantation in III–V technology it is important to point out the successful application of the said technique to achieve mixing of superlattice structures with a view to carve nanostructures in the lateral substrate plane (Venkatesan *et al* 1986; Hiramoto *et al* 1987; Schwarz *et al* 1987). This application essentially makes use of the ion-beam mixing method and it has already been demonstrated to be useful in the synthesis of quantum boxes (QB) and quantum well wires (QWW) (Hiramoto *et al* 1987). An outcome of these studies on the fundamental side is the observation of a critical role played by defect–defect and impurity–defect interactions in governing the mixing process and its uniformity (Venkatesan *et al* 1986; Schwarz *et al* 1987). This once again emphasizes that implantation in III–V semiconductors offers a rich class of scientific phenomena which have a direct implication on technology, thus making this area an interesting ground for innovative research.

Having discussed the outstanding issues related to ion implantation in III–V compound semiconductors we now turn to the discussion about damage annealing in these materials, which forms another area. In advanced semiconducting technologies presently anchored to silicon as the base material, damage annealing is achieved by thermal treatment or by usage of pulsed and continuous wave (CW) lasers or electron beams, the use of *e*-beam being less common for this objective and more common for submicron lithography. Thermal treatment schemes for annealing of damage in III–V semiconductors in general and GaAs in particular face severe difficulties in view of the structural instabilities in these materials which lead to out-diffusion of specific atomic species leading to the generation of a host of defects and defect complexes. Unfortunately the temperature range at which fruitful annealing and dopant activation effects can be realized is also the temperature range at which surface-related structural instabilities set in and, hence, unless clever tricks are employed the conventional simplistic thermal treatment is not likely to be successful in the context of III–V semiconductors. Some such tricks which have been attempted in the past and have met with partial success included capped-annealing (Pearson and Cummings 1980), proximity-annealing (Molnar 1980) or annealing in an overpressure of the out-diffusing species (Woodhouse *et al* 1987). In capped-annealing an attempt is made to deposit a high density, non-porous, structurally stable nitride or oxide layer on GaAs prior to annealing treatment so as to arrest the As out-diffusion process at its origin. However, in most cases the caps either crack during thermal treatment at elevated temperature or they are not adequately adherent and the scheme does not succeed to the extent expected. Also the strain- and defect-induced electronic states at the interface lead to unwanted effects in carrier transport and optical phenomena such as luminescence linewidth and efficiency which are critical to the performance of a device based on these materials. Further, the choice of the cap material cannot be completely arbitrary since it has to be compatible with the further process steps. In proximity-annealing a GaAs

wafer is kept in close proximity with the surface of a wafer being processed and a local overpressure is generated with a view to thermodynamically counter the out-diffusion process. Overpressure can also be generated without the proximity scheme by an external source but these schemes also have been found to be of limited use. The newer proposals in the context of annealing centre around the use of rapid thermal annealing (RTA) (Davis 1985; Sugitani *et al* 1987) or laser annealing (Wood and Young 1984; Nissim and Gibbons 1984).

The notion of rapid thermal annealing (RTA) or rapid thermal processing (RTP) relies on the fact that for annealing of local structural defects or atomic disorder long range atomic transport is unnecessary; and suppression of such transport in an annealing scheme can arrest growth of global instabilities. The RTA process has been generally demonstrated to be superior to conventional thermal annealing in a number of situations of interest. Also RTP has been used for precise control of length scale in interface reactions. Both these processes have now become an integral part of III-V compound semiconductor-based device research.

Laser can be used for annealing purposes in two modes viz. scanned CW mode (Lowndes 1984) or pulsed mode (Wood and Young 1984). In the case of GaAs the room temperature band-gap is 1.42 eV which corresponds to 800 nm on the wavelength scale. There are several choices of laser available for use with this and other III-V compound semiconductors. Amongst CW lasers one can use an Ar⁺ laser ($\lambda = 488$ nm; 515 nm) or a Na : YAG laser ($\lambda = 1.06$ μ m, 530 nm with frequency doubling); while amongst pulsed lasers one can use a ruby laser ($\lambda = 694.5$ nm, $t = 30$ ns, energy per pulse = few joules) or an excimer laser ($\lambda = 192$ nm, 248 nm or 308 nm, $t = 20$ ns). Excimer lasers are becoming more common in such annealing technologies because they operate in the UV range and have a high pulse repetition rate of up to 100 Hz.

CW lasers used for annealing have power equivalent to a few watts and are focussed down to a spot size of 50 to 100 μ m to enhance power density. The spot is then scanned over the surface at a speed of 1 to 30 cm/s which leads to a dwell time at a location of about 0.1 to 10 ms. This time is enough for the heat to diffuse below the implantation-induced damaged region but is not very large for impurity redistribution, especially since the regrowth in this case occurs in the solid phase i.e. without melting. The temperature time product critically controls annealing or processing by CW lasers. It has been found that this aspect of CW-laser processing is especially useful for damage-annealing and dopant activation. On the other hand, pulsed lasers which generally operate at power densities leading to melting are more effective in damage-annealing but not in alloying of contacts. In the latter context pulsed lasers do not appear suitable because they lead to segregation/precipitation effects and attendant non-uniformities. It is clear that a significant amount of research effort based on innovative ideas is needed to make the intrinsically advantageous features of lasers available for beneficial use in III-V compound semiconductor technology.

3. Conclusions

In conclusion, it can be stated that ion implantation and laser treatment studies on GaAs and other III-V compound semiconductors are, scientifically as well as

technologically extremely important areas of research which offers a number of avenues for innovative and useful ideas.

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