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Laser processing of III–V compound semiconductors

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Abstract. Lasers have found an increasingly important role in semiconductor processing technology. While they are now widely used in some of the silicon-based device fabrication processes, their applications in III–V compound semiconductor processing are not equally well established. Considerable research work has been carried out to find ways to overcome some of the technical difficulties in their usage in technologies based mainly on GaAs. In this paper, we review these developments and mention possible future directions that will help establish the use of lasers in this very active field.

Keywords. III–V Compound semiconductors; device technology; implantations; ohmic contacts; laser annealing.

1. Introduction

Modern techniques in semiconductor device fabrication processes have revolutionized the world of electronics. Semiconductor devices have now a very large range of applications and are available in a variety of forms from a single device, e.g. a high-power rectifier diode, to a computer memory circuit with over a million devices integrated on a chip. The success of these developments is mainly due to the suitability of silicon and its thermally grown stable oxide in the planar technology. The interest in III–V compound semiconductors like GaAs has been growing because of the high frequency and high speed operations of devices possible here (Wisseman and Frensley 1985). Also, many of these materials, unlike Si, are suitable for optoelectronic applications such as lasers and light emitting diodes. On the other hand, the lack of a good native oxide and the surface instabilities at elevated temperatures (e.g. loss of group V elements) necessitate a departure in techniques from the planar technology used for Si. Thus, very special care is needed to avoid problems like surface decomposition and non-ohmic contacts and to obtain predictable impurity profiles during any thermal treatment step in GaAs processing. Techniques like ion implantation, closed tube thermal annealing in excess As vapour pressure, encapsulating layer depositions, Schottky contacts for gates and rapid thermal annealing using lamps have been used in attempts to achieve an acceptable quality of the finished devices. With this, several applications, e.g. Gunn diode, monolithic microwave integrated circuits (MMIC) and lasers, have been demonstrated.

Just as high-power lasers, with their capability of delivering thermal energy in a controlled domain of space-time, have been successfully used in Si technology (Gibbons 1984; Wood and Young 1984) for achieving spacially selective thermal treatments of surfaces, as in, for example, impurity redistribution, damage removal and recrystallization applications, it would be of great interest to investigate whether some of the complex thermal steps used in GaAs technology can be sub-

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stituted by simpler laser processing in an advantageous manner. In order to do this, it is useful to first make a brief survey of the standard GaAs device processing and identify the thermal steps used in this.

1.1 *A typical III–V device fabrication procedure*

A sequence of process steps used in making a GaAs-based transistor (Abe *et al* 1985) is shown in figure 1. The substrate is semi-insulating GaAs ($\rho \sim 10^8 \Omega$ cm) or an undoped liquid phase epitaxial (LPE) buffer layer on it. Defining a device area by opening a window in an insulator overlayer deposited on the substrate, a channel implantation, typically of Se^+, is carried out at 100 to 200 keV with a dose of 10^{12} to 10^{13} cm^{-2}. The expected range of implant is about 0·2 μm and the doping (n-type) is 10^{17} cm^{-3}, giving a sheet resistivity of $\rho_\square = 200\ \Omega/\square$. As shown in figure 1c, a second masking defines a region for another implantation, typically of Si^+ at 400 keV with a dose of 10^{14} to 10^{15} cm^{-2}, to produce a low-resistivity ($\rho_\square \sim 50\ \Omega/\square$) area for achieving a good ohmic contact to the metal, to be deposited later. A thermal anneal process is required to remove the implantation damage and to electrically activate the implanted donor atoms. To avoid As loss during this step, typically carried out in furnaces at 600°C to 900°C for 5 to 30 min, either an encapsulating layer or a closed tube treatment in presence of excess As vapour pressure is used. This adds to the complexity of the fabrication process. Also the overlayer often reacts with the substrate beneath, causing a deterioration of the surface. To achieve recrystallization, substitution of donor atoms at proper sites (Se at As, Si at Ga sites) and maintenance of the stoichiometry (no antisite defects like Ga on As sites etc.), this thermal step has to be followed very carefully. Also a global heating of the whole substrate can mobilize some of the other impurity atoms present in the bulk, e.g. Cr, used to achieve compensation (i.e. high ρ). The effects of this have to be avoided. Figure 1e shows the metal deposition through

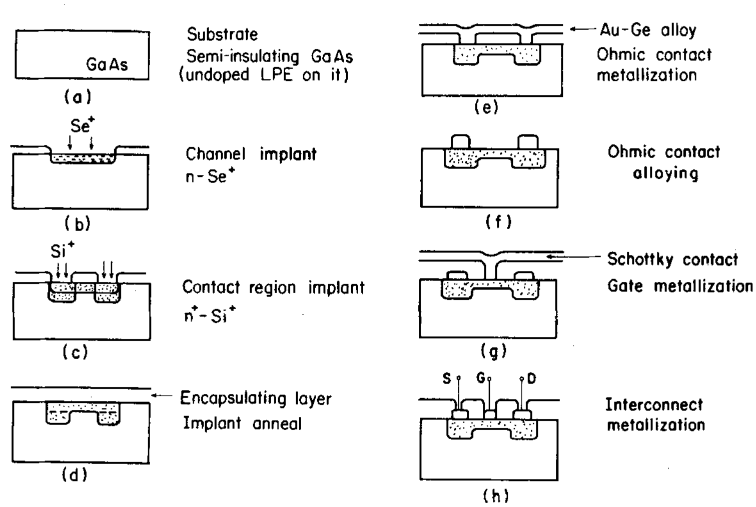

Figure 1. Typical sequence (**a–h**) of process steps in a GaAs device fabrication. Note that there are two major thermal steps in this: (1) implantation anneal; (2) alloy ohmic contact.

windows in insulator film to make ohmic contacts to the n^+ regions. Typically, a composition of Au–Ge (88% gold, 12% germanium) is used. The Au–Ge eutectic melts at 357°C. To form a good ohmic contact, the wafer is heated to 450°C for about 30 sec in H_2 or forming gas. At this temperature, Ge dopes GaAs to give n^+ GaAs surface and Au makes an ohmic contact to that, giving a small contact resistance ($\rho_c \sim 10^{-6}\,\Omega\,\mathrm{cm}^{-2}$). This is a very critical thermal step as small deviations from the optimal procedure lead to rough surfaces, high contact resistances, etc. Finally a Schottky gate contact using Al or Ti–Pt–Au layers is used to obtain a finished device (figures 1 g and h).

It is thus seen that the procedure has two important thermal steps: 1) implantation anneal, and 2) alloy ohmic contact.

In view of the very special care necessary to achieve them in furnaces and the associated disadvantages such as (1) unnecessary global heating, (2) As loss, (3) critical temperature–time cycles, and (4) surface deterioration is of much interest to study the suitability of lasers in replacing these furnace treatments. With the special advantage of lasers in achieving localized surface heating in a short time without disturbing the substrate, they hold great promise in simplifying the III–V compound semiconductor processing while making the procedure reliable and reproducible.

Before one contemplates using the lasers in the above processing, it is necessary to understand the thermal processes a laser beam initiates in III–V materials, so that the desired temperature–time cycle can be designed based on laser parameters such as beam power, photon energy, repetition rate, etc. In the next section, we briefly discuss these aspects and the considerations required for a proper selection of the laser parameters.

2. Preliminary considerations

Many III–V semiconductors like GaAs have a direct band gap (E_g). When a photon of energy $h\nu$ falls on the surface of such materials, the dominant absorption mechanism depends upon the following factors. If $h\nu < E_g$, a direct photon–lattice coupling may occur, if $h\nu$ is comparable with the vibrational energies. Near the band gap $h\nu \lesssim E_g$, absorption occurs via the tail states near the band edges. This can be important for noncrystalline surfaces. For $h\nu > E_g$, there is a valence to conduction band transition, creating hot electron hole pairs which lose energy to the lattice by emitting phonons on a time scale of a few picoseconds. At high-power excitations, nonlinear effects such as multiphoton absorption etc. become important. Finally the carriers undergo nonradiative or radiative recombinations giving up the resultant energy to the lattice on a nanosecond time scale. The coefficient of photon absorption and the temperature rise in GaAs-like semiconductors depends upon the above energy loss mechanism. Also their relative importance may be time-dependent. For example, an initially amorphous layer may become crystalline during the photon beam energy absorption. The important factors in the above considerations are $h\nu$, the substrate temperature T_s, lattice crystallinity and the semiconductor band structure. The heat flow in the material is governed by the equation

$$\rho C \frac{\partial T}{\partial t} - \vec{\nabla}\cdot(K\vec{\nabla}T) = P(\vec{r}, t),$$

where ρ is mass density, C is specific heat, K is thermal conductivity and D is diffusivity ($=K/C\rho$). P, the heat source term, depends on the light$\rightarrow$heat conversion in the semiconductor. The parameters ρ, C, K in turn can be functions of the temperature T. In the event in which the surface melts in a few picoseconds, a different formulation based on, for example, finite differences is often used. A detailed discussion of the heat flow equations can be found elsewhere (Wood and Jellison 1984) and will not be given here. It should, however, be mentioned here that a calculation of the surface temperature, given the laser and material parameters, is very useful for designing the experimental conditions of laser treatment.

Another aspect to be mentioned here concerns the choice of laser for a thermal treatment. A consideration of CW versus pulsed lasers and of parameters like repetition rate, photon energy $h\nu$, beam power profile (size, shape), beam power, scan speed, etc. is required before an experiment is undertaken.

In the case of GaAs ($E_g \cong 1{\cdot}42$ eV at 300 K, corresponding to $\lambda_g \sim 800$ nm) some of the choices available are as follows: (1) CW lasers: Ar^+ laser ($\lambda = 488$ nm, 515 nm), Nd–YAG laser (at $\lambda = 1{\cdot}06\ \mu$m or $\lambda = 530$ nm with frequency doubling). These have a CW beam power of a few watts so that the scanning of a focused beam over the substrate is essential. (2) Pulsed lasers: Ruby ($\lambda = 694$ nm, beam size of about 2 mm × 4 mm, pulse width of a few nsec, repetition rate of a few Hz with power densities ε of a few MW/cm^2), Nd–YAG ($\lambda = 1{\cdot}06\ \mu$m or 530 nm, ε of a few MW/cm^2 with a pulse width of tens of nsec). Also, recently, excimer lasers (with a broad beam, typically 3 mm × 15 mm, high power of over 200 mJ/pulse at $\lambda \sim 248$ or 308 nm with pulse width of a few nsec and repetition rate of about 100 Hz) have become available.

Some of these have been used to perform the thermal treatments in GaAs processing, as discussed in the following sections which review the results obtained on laser applications for annealing implantation damage and to obtain good ohmic contact.

3. Implantation annealing in GaAs

Typical conditions used for implantations in GaAs are as follows: (1) ions: S, Se, Te, Si, Sn (n type) and Cd, Be, Zn, Mg (p type), (2) energies: 100–400 keV, (3) range: 0·2–0·4 μm, (4) dose: 10^{12}–10^{13} cm^{-2} (channel region), 10^{14} cm^{-2} (contact region). The implantations can lead to short-range disorder (such as non-stoichiometry) and large-range disorder (such as amorphosity). The annealing is required to achieve (1) crystallization, (2) stoichiometry, and (3) donor atoms at proper sites, so that the impurities are electrically activated and the carrier mobility is sufficiently high. Also the thermal annealing should avoid (1) surface decomposition (e.g. loss of As atoms), (2) change in properties of the bulk substrate, (3) reaction with the overlayer (e.g. Si_3N_4 encapsulating layer), and (4) oxide formation (e.g. Ga_2O_3 layer).

The quality of the annealed surface can be assessed by various techniques such as (1) Rutherford back scattering (RBS), (2) transmission electron microscopy (TEM), (3) Auger or secondary ion mass spectroscopy (SIMS) profiling, (4) photoluminescence, (5) electrical measurements like current–voltage, capacitance–voltage, Hall and van der Pauw measurements, (6) Raman scattering, etc.

Such experiments have been performed on implanted GaAs with CW or pulsed laser annealing. We consider these two cases separately.

3.1 *CW laser annealing*

In this case, the high power density required to achieve damage annealing has to be attained by focusing the beam with a lens to a spot, typically of 50 μm to 100 μm in size. To obtain thermal treatment of a large area (say a few cm^2), it is necessary that the beam should be scanned over the implanted area, at a speed V, typically 1 to 20 cm/sec. This leads to a dwell time t_w (= spot size/v) of about 0·1 to 10 msec. Such a time is large enough for the generated heat to diffuse well below the damaged layer, which is, typically, less than 1 μm in depth. However, t_w is small for impurity distribution. The regrowth of a smooth surface, in the case of CW annealing, is by solid-phase epitaxy (no melting). For this, the surface temperature θ_s is a crucial factor. This in turn is governed by t_w and the beam power density. Computational models to obtain θ_s with corrections due to temperature dependence of material parameters ρ, K and C, finite sample thickness, substrate temperature, etc. are available (Lax 1977). Unlike in the case of Si, the scale for the calculated θ_s versus beam power P cannot be easily fixed in the case of GaAs by the two points (T_{melt}, P_{melt}) and ($T_{substrate}$, $P = 0$). This is due to the fact that the thermal decomposition with a loss of As atoms occurs well before the melting temperature of GaAs ($\sim$1235°C). With a round spot, it has been found that the sharp thermal gradients in directions perpendicular to the scanning lead to slip lines and other defects in the case of GaAs. This problem can be avoided by using a beam with an elliptical cross-section obtained with the help of a cylindrical lens. The scanning is done along the minor axis of this beam spot. The other method tried to prevent thermal shock in GaAs is to use a high substrate temperature of 580°C (Fan *et al* 1979) during the CW laser scanning.

In the case of heavy implantations (of dose $> 10^{14}$ cm^{-2}) which lead to surface amorphization, it was found by Fan *et al* (1979) that if the beam power–scan speed combination was such that the surface temperature was below the threshold for producing slip lines, the electrical activation was only partial ($< 30\%$) while the mobility was also not satisfactory (< 2000 cm^2/Vsec). As the power was increased to achieve better activation, surface deterioration and slip line formation occurred, leading to even lower mobility. Other studies (Anderson *et al* 1980; Olson *et al* 1980; Williams and Harrison 1981) have also indicated that a CW laser power window for obtaining good lattice order and donor substitution without causing slip lines and cracking does not exist for GaAs. For low dose implantations ($\lesssim 10^{13}$ cm^{-2}), it has been found (Nissim and Gibbons 1981) that formation of a thin oxide layer (Ga_2O_3) during annealing in O_2 environment helps in achieving nearly 100% electrical activation. The mobility, however, was still low ($\sim$1800 cm^2/Vsec), presumably due to poor interface between the oxide layer and GaAs surface. As summarized by Nissim and Gibbons (1984), the regrowth of damaged GaAs by solid-phase epitaxy is not well understood yet and considerable work remains to be done to fully explore the CW laser annealing of ion implanted GaAs.

3.2 *Pulsed laser annealing*

In this case, the laser beam is often broad (about a few mm^2). The dwell time t_w is typically in the nanosecond time scale. Such a value is not enough for the heat to diffuse and redistribute during the pulse duration. It is also not enough for solid phase regrowth. In such a case, regrowth is achieved by increasing the power to obtain a molten surface layer of a depth greater than that of the damaged region ($\sim 0{\cdot}5\ \mu m$). The melting remains for hundreds of nanoseconds. During that time, the liquid–solid interface moves towards the top surface at a velocity of 300 cm/sec or so. Thus the annealing and regrowth is by an ultrarapid liquid-phase epitaxy (LPE).

The questions relevant to GaAs processing using pulsed lasers are: (1) What is the threshold in power to obtain a molten surface? (2) Is the As loss during the LPE time significant? (3) Does LPE lead to impurity redistribution? (4) Are there new segregation effects due to non-equilibrium during the rapid cooling? (5) Does the rapid solidification lead to quenching of defects and to non-stoichiometry? (6) How good is the donor substitution and electrical activation? Answers to some of these questions are now known and are reviewed in great detail by Lowndes (1984). Briefly, we may summarize these results as follows.

(1) The threshold in energy density for damage in GaAs is $0{\cdot}8\ J\ cm^{-2}$ while the melting begins to occur at a much lower density of $0{\cdot}2\ J\ cm^{-2}$. In this case, the melt depth is about 20 nm for photons with $\lambda = 533$ nm.

(2) Equilibrium vapour pressure of As at the melting temperature of GaAs is about 1 bar. This corresponds to an As loss of about one monolayer/5 nsec. Evidence for As loss and Ga-rich surfaces after pulsed laser annealing is found in RBS and TEM experiments. (If Te doping is used, it partly reduces the effects of As loss by occupying As sites.)

(3) Implanted impurity profiles change and deeper distributions occur after the regrowth because of melting. Also it has been found that the segregation coefficient (ratio of solute density in liquid to that in solid) is larger than known values at equilibrium.

(4) It has been found by RBS channeling experiments that lattice point substitutionality after pulsed laser melting treatment is very good and is far superior to CW laser regrowth. The As loss however leads to quenched vacancy formation and antisite defects. Also, if the melt depth is not greater than the damage depth and if the damage leads only to polycrystallinity rather than amorphization, then there is a poor quality regrowth. Hence, pulsed laser annealing is not effective for low-dose implantation.

(5) The conventional furnace anneal with encapsulant layer (of, e.g. Si_3N_4) is usually done at temperatures above 600°C for over 5 min. Although this leads to acceptable electrical activation (over 50%) and mobility values ($\sim 2000\ cm^2/Vsec$), there are difficulties related to impurity–encapsulant reactions and to defect formation. With a pulsed laser anneal, it has been found that while the activation after a heavy implant dose is reasonably good (up to 50%), the mobility values are low ($\sim 1000\ cm^2/Vsec$). These results are presumably related to antisite substitution and/or compensation. For low implant dose ($< 10^{14}\ cm^2$), the pulsed laser has not been successful.

Further research is necessary to improve pulsed laser treatment to anneal out implantation damage.

4. Alloying Au–Ge contacts to GaAs

The conventional technique of forming ohmic contacts to n-GaAs consists of the evaporation and subsequent thermal alloying of a layer of eutectic composition of Au–Ge (Braslaw *et al* 1967). This method often leads to (1) surface roughness, (2) poor edge definition, (3) microprecipitates of non-uniform composition, and (4) uneven penetration into GaAs. It requires critical temperature–time control to prevent Ge going to As sites (making the GaAs less *n* type) and the loss of As dissolved in the Au–Ge melt. A rapid thermal heating (50°C/sec) for short times has been found useful. The advantage of lasers in producing high surface temperature for short times is therefore expected to be important. Both CW and pulsed laser treatments have been tried in the past.

A comparison of different beam irradiation techniques for alloying Au–Ge contacts on GaAs has been reported by Eckhardt (1980). The best results have been obtained in the case of a CW Ar^+ laser. Gold *et al* (1979) used a focused CW Ar^+ laser beam of 2·5 W with a 40 μm spot and scanned it at 12·5 cm/sec over a multilayer of Au (300 Å) and Ge (100 Å), sometimes with a thin (20 Å) layer of Ni on GaAs. The results are satisfactory, giving $\rho_c \sim 10^{-6}\,\Omega\,cm^{-2}$. Auger spectroscopy shows that there is little metal–semiconductor interdiffusion and the surface is smooth. Gold *et al* (1979) have also used a free-running ruby laser at 1·5 J cm^{-2} with a long pulse width of over 1 msec. The results are comparable to those obtained with CW Ar^+ laser. Such success is not obtained for pulsed lasers with short pulses. The ρ_c is large and the results are irreproducible in these cases.

5. Concluding remarks

It appears that although much work has been done to study laser processing of III–V compound semiconductors (mainly GaAs), the techniques need to be perfected and further evaluated using variations of other factors, such as the effects of an oxide or other encapsulant layers, or presence of different ambient gases, etc. The use of high-power pulsed lasers to anneal the damage due to heavy-dose implantations and of CW lasers to make ohmic alloy contacts seems to have been rather successful. The other application of lasers, viz. to obtain impurity diffusion into GaAs from a deposited film, is very interesting. Tin-based coating ($SnO_2 + SiO_2$, Emulsitone film with ethyl alcohol binder, spin-coated on GaAs) has been used to obtain Sn doping of GaAs with the help of a CW Ar^+ treatment (Nissim and Gibbons 1984). It would be interesting to see if such methods can be used in the case of other dopants. Also, laser-activated diffusion of implanted impurities and the modelling of the distribution profiles is another possible area of research. The use of new lasers (e.g. excimer) for III–V semiconductor processing is also under investigation currently. Further work should establish the role of lasers in this area to the extent similar to that in the field of Si processing.

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